Electronic and magnetic properties of $LaV_{1-x}O_3$

by

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Abstract

A series of $LaV_{1-x}O_3$ compounds ($x=0.00$, 0.02, 0.04, 0.06, 0.08) were prepared using the standard solid reaction. The samples were characterized by X-ray diffraction (XRD), four-probe resistivity, and magnetic susceptibility studies.

Powder X-ray diffraction analysis indicated the formation of a single-phase sample with an orthorhombic structure which was first found in $GdFeO_3$ (space group $Pnma$). The Unit Cell program was used for calculating lattice parameters from XRD data. The XRD spectrum could be indexed on a cubic lattice with $a_c = 2a_p \approx (7.8578$ to $7.9414 \text{Å})$. The lattice parameter was observed to increase as the Vanadium vacancy increased.

Four-probe resistivity measurements exhibited semiconductor behavior for all samples from room temperature down to 19K. The resistivity of samples increased with increasing Vanadium vacancy. The resistivity of samples demonstrated activated conduction with an activation energy of approximately 0.2 eV. The activation energy increased with increasing lattice parameter.

Field cool magnetic susceptibility measurements were performed with field of 500 G from 300 K to 5 K. These measurements indicated the presence of an antiferromagnetic transition at about 140 K. The data was fitted above Néel temperature to Curie-Weiss law yielding a negative paramagnetic Curie temperature. This implies that antiferromagnetic ordering is present.
Contents

Abstract ................................................................. ii

Contents ................................................................. iii

List of Tables ............................................................ v

List of Figures ............................................................ vi

Acknowledgements ......................................................... viii

1 Introduction .............................................................. 1

2 Method of preparation ................................................... 8
   2.1 Preparation of the ceramic samples of $LaV_{1-x}O_3$ .................. 8
   2.2 X-ray diffraction .................................................. 8

3 Resistivity ............................................................... 16
   3.1 Temperature dependence of resistivity .................................. 16
      3.1.1 Metal ......................................................... 16
      3.1.2 Semiconductor ................................................. 17
   3.2 Experimental Procedure ............................................. 18
      3.2.1 Four probe resistivity measurement .......................... 18
      3.2.2 Preparation for resistivity measurement ...................... 19
   3.3 Resistivity of $LaV_{1-x}O_3$ ....................................... 19
Contents

4 Magnetization

4.1 Magnetism

4.1.1 Diamagnetism

4.1.2 Paramagnetism

4.1.3 Ferromagnetic

4.1.4 Ferrimagnetism

4.1.5 Antiferromagnetism

4.2 Experimental procedure

4.2.1 SQUID

4.2.2 DC Magnetometry

4.2.3 AC Magnetometry

4.3 Magnetization of ceramic sample $LaV_{1-x}O_3$

5 Conclusions

Bibliography
List of Tables

2.1 Lattice Parameter of Samples, calculated by Unit Cell Program .................. 15

3.1 Energy gap and lattice parameter of $LaV_{1-x}O_3$ ................................. 27

4.1 Summary of different magnetic materials. .................................................. 32

4.2 Values of the Néel temperature $T_N$, the paramagnetic Curie temperature $\theta$
and molar Curie constant $C_M$, for $LaV_{1-x}O_3$ as obtained by this work and
other workers.  ............................................................................................... 41
List of Figures

1.1 Perovskite structure ................................................. 3
1.2 High $T_C$ superconductivity ..................................... 4
1.3 Antiferromagnetic behavior of $La VO_3$ ......................... 4
1.4 $d^2$ electronic structure of vanadium in $La VO_3$ .............. 5
1.5 Temperature dependence of resistivity in $La_{1-x} Sr_x VO_3$ .... 6
1.6 Plots of resistivity versus temperature for representative $LaTi_{1-x} V_x O_3$ phases. 7

2.1 Expected X-ray Diffraction spectrum for $La VO_3$ generated by Unit Cell Program 9
2.2 hkl index of the x-ray peaks for $La VO_3$ ........................ 10
2.3 X-ray Diffraction spectrum for $La V_{0.98} O_3$ .................. 11
2.4 X-ray Diffraction spectrum for $La V_{0.96} O_3$ .................. 12
2.5 X-ray Diffraction spectrum for $La V_{0.94} O_3$ .................. 13
2.6 X-ray Diffraction spectrum for $La V_{0.92} O_3$ .................. 14

3.1 Semiconductor band energy ........................................... 17
3.2 Four-probe method ................................................... 19
3.3 Resistivity of $La V_{1-x} O_3$ ....................................... 20
3.4 Resistivity of $La VO_3$ .............................................. 21
3.5 Resistivity of $La V_{0.98} O_3$ ...................................... 22
3.6 Resistivity of $La V_{0.96} O_3$ ...................................... 23
3.7 Resistivity of $La V_{0.94} O_3$ ...................................... 24
3.8 Resistivity of $La V_{0.92} O_3$ ...................................... 25
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>Energy gap versus lattice parameter</td>
<td>26</td>
</tr>
<tr>
<td>4.1</td>
<td>Diamagnetism</td>
<td>29</td>
</tr>
<tr>
<td>4.2</td>
<td>Paramagnetism</td>
<td>30</td>
</tr>
<tr>
<td>4.3</td>
<td>Ferromagnetism</td>
<td>31</td>
</tr>
<tr>
<td>4.4</td>
<td>Type of magnetism</td>
<td>33</td>
</tr>
<tr>
<td>4.5</td>
<td>Superconducting quantum interference device as a simple magnetometer</td>
<td>36</td>
</tr>
<tr>
<td>4.6</td>
<td>SQUID SCHEMA</td>
<td>36</td>
</tr>
<tr>
<td>4.7</td>
<td>MPMS SQUID</td>
<td>37</td>
</tr>
<tr>
<td>4.8</td>
<td>The magnetic susceptibility of $LaV_{1-x}O_3$</td>
<td>39</td>
</tr>
<tr>
<td>4.9</td>
<td>Inverse of Susceptibility of $LaV_{1-x}O_3$</td>
<td>40</td>
</tr>
</tbody>
</table>
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Last but never the least, I am thankful for the warm support of my family. I would like to dedicate my thesis to my parents, this is for you.
Chapter 1

Introduction

There have been many studies of transition-metal oxides (TM)\(^1\) \(ABO_3\), both experimental and theoretical, due to their wide variety of electronic and magnetic properties. The discovery of high-\(T_C\) superconductivity in layered cuprates has attracted attention on the electronic state of TM oxides [6]. The oxides with perovskite-related structures, Fig. 1.1, have been studied intensively because the layered-perovskite structure is believed to be responsible for high-\(T_C\) superconductivity. It is now well known that the high-\(T_C\) superconductivity occurs when extra holes or electrons are introduced into the parent antiferromagnetic insulators by the cation substitution or by controlling the oxygen content. This is usually called "carrier doping", Fig. 1.2 [22]. Most of the transition-metal oxides have the perovskite structure which allows for doping of charge carriers by chemical heterovalent substitutions over a wide range of compositions without breaking the structural network. It has also been found that most of the latest TM insulating oxides such as Ni and Cu oxides are so-called charge-transfer insulators where the lowest charge excitation is from oxygen 2p to metal 3d state [33]. This is contrasted with earlier TM oxides such as Ti or V oxides where the band gaps are mostly Mott-Hubbard insulators. In a Mott-Hubbard insulator, the lowest energy gap is between upper and lower Hubbard bands [14]. Both Hubbard bands are transition-metal based d states that arise from Electron-Electron correlation. An equivalent description using the Goodenough model [16] attributes the gap in a Mott-Hubbard insulator to valence fluctuation or charge disproportionation of the transition metal ions; \(d^n + d^m \rightarrow d^{n+1} + d^{m-1}\).

\(^1\)An element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell.
The energy of this process is defined as the electron correlation energy.

$LaVO_3$ has attracted great scientific interest for more than fifty years [7]. After many studies of electronic and magnetic properties of $LaVO_3$, the exact description of these properties has not been found. In all the experimental and theoretical works, it is agreed that $LaVO_3$ is an insulating antiferromagnet with the Néel Temperature, $T_N$, of 135-140 K, Fig. 1.3 [23, 30, 27]. The basis for all theories is the description of the $V^{3+}$ ion (2 d electrons) and their electronic structure in the perovskite crystallographic structure, Fig. 1.4. The compound $LaVO_3$ has a distorted perovskite structure having the orthorhombic arrangement first found in $GdFeO_3$ (Space group $Pbnm$) above $T_N$. In the perovskite based structure of $LaVO_3$ the vanadium ions are placed in a distorted oxygen octahedron, Fig. 1.1-b.

The antiferromagnetic (AF) order of V moments was confirmed using neutron scattering experiments [6] and $^{51}V$ NMR measurements. [21, 20, 23]. A Curie-Weiss fit to the data above $T_N$ yields a negative paramagnetic Curie temperature indicative of antiferromagnetic ordering. The saturation moment at 4.2 K, as obtained from a neutron-diffraction investigation [23] was found to be $1.3\pm 0.1 \mu_B$, which is much less than the spin-only moment ($2\mu_B$) expected for a $S=1$ system such as $V^{3+}$, with $g=2$. Dougier and Hagenmuller[23] found that $LaVO_3$ exhibited weak ferromagnetism below $T_N$. Several authors have reported that $LaVO_3$ shows a large negative remanence below $T_N$ if the samples are cooled in an external magnetic field below 1kG. [23, 27, 21]

The study of Metal-Insulator(M-I) transition in transition-metal oxides is of current interest to the solid-state chemistry and physics communities. It is known that $LaVO_3$ exhibits a M-I transition by substitution of Sr for La at a Sr concentration of about 0.2 \(^2\) and substitution of Ti for V at Ti concentration of 0.1-0.25 \(^3\) as seen in Fig. 1.5 and Fig. 1.6, respectively.

\(^2\)[24]
\(^3\)[12]
Figure 1.1: **Perovskite structure** $ABO_3$. The ideal $ABO_3$ perovskite structure is cubic (a), but other structure types such as tetragonal, orthorhombic (b) etc. are also possible due to distortion of the octahedra $BO_6$ (c) itself or tilting of the octahedra. [1]
Figure 1.2: High-$T_C$ superconductivity occurs when extra holes or electrons are introduced into the parent antiferromagnetic insulators. [2]

Figure 1.3: Antiferromagnetic behavior of $LaVO_3$. 
Figure 1.4: Lowest part of the electronic structure of the $d^2$ orbitals in $LaVO_3$ in the strongly-correlated limit. a) Hund's rules ground terms, b) effect of the octahedral Crystalline Electric Field (CEF) interactions, c) the many-electron CEF states in the octahedral CEF in the presence of the intra-atomic spin-orbit coupling, d) Simplified electronic structures. [30]
Figure 1.5: Temperature dependence of the resistivity in $La_{1-x}Sr_xVO_3$ [24]
Figure 1.6: Plots of resistivity versus temperature for representative $LaTi_{1-x}V_xO_3$ phases [12]

Four-probe resistivity measurements on single crystals exhibited activated conduction with an activation energy of 0.14 eV [25]. It should be noted that this estimate of the transport gap is about one order of magnitude smaller than the intrinsic Mott-Hubbard gap in $LaVO_3$ which is 1.1 eV estimated from optical spectroscopy [17].
Chapter 2

Method of preparation

2.1 Preparation of the ceramic samples of $LaV_{1-x}O_3$

Polycrystalline samples of $LaV_{1-x}O_3$ ($x=0.00, 0.02, 0.04, 0.06, 0.08$) were prepared by standard solid reaction. Samples were synthesized by mixing stoichiometric amounts of high-purity $La_2O_3$ (99.998% Alfa Aesar) and $V_2O_5$ (99.998% Alfa Aesar) powders by using mortar and pestle. This mixture was then pressed into pellets by applying a force of approximately 10 metric tons using a stainless steel die with 13mm diameter. The pressed pellets with a thickness of approximately 1-4mm, were typically sintered at 950 °C for 2 hours in flowing He(95%) and $H_2$(5%). The pellets were reground, repelletized, and sintered again for about 30 hours at 1100 °C in flowing He(95%) and $H_2$(5%). $LaV_{1-x}O_3$ samples were obtained by hydrogen reduction of these $LaV_{1-x}O_4$ samples by heating at 950 °C for 12 hours an atmosphere of 8.5% $H_2$ and 91.5% He.

2.2 X-ray diffraction

To characterize the samples and ascertain their quality, X-ray powder diffraction was performed on all the samples using Cu $K_\alpha$ radiation. In this work we used The International Center for Diffraction Data (ICDD)$^1$ PDF files and the data that we generated by the Powder Cell Program$^2$, Fig. 2.1, to find the (hkl) indices of the peaks, Fig. 2.2.

$^1$[13]
$^2$[28]
Chapter 2. Method of preparation

Figure 2.1: Expected position of the peaks calculated by Unit Cell Program
Figure 2.2: hkl indices of the peaks for $LaVO_3$
Figure 2.3: X-ray Diffraction spectrum for $LaV_{0.98}O_3$
Figure 2.4: X-ray Diffraction spectrum for $LaV_{0.96}O_3$
Figure 2.5: X-ray Diffraction spectrum for $LaV_{0.94}O_3$
Figure 2.6: X-ray Diffraction spectrum for \( \text{LaV}_{0.92}\text{O}_3 \)
Chapter 2. Method of preparation

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å) ±0.005</th>
<th>b (Å) ±0.005</th>
<th>c (Å) ±0.005</th>
<th>a/√2 ±0.003</th>
<th>b/√2 ±0.003</th>
<th>c/2 ±0.002</th>
<th>a_p ±0.002</th>
<th>a_c ±0.002</th>
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</thead>
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<tr>
<td>LaVO₃</td>
<td>5.557</td>
<td>5.566</td>
<td>7.842</td>
<td>3.930</td>
<td>3.936</td>
<td>3.921</td>
<td>3.929</td>
<td>7.858</td>
</tr>
<tr>
<td>LaV₀.₉₈O₃</td>
<td>5.566</td>
<td>5.613</td>
<td>7.920</td>
<td>3.936</td>
<td>3.969</td>
<td>3.960</td>
<td>3.955</td>
<td>7.909</td>
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<td>5.651</td>
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<td>3.996</td>
<td>3.961</td>
<td>3.965</td>
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<td>LaV₀.₉₄O₃</td>
<td>5.565</td>
<td>5.628</td>
<td>7.925</td>
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<td>3.980</td>
<td>3.960</td>
<td>3.959</td>
<td>7.918</td>
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<tr>
<td>LaV₀.₉₂O₃</td>
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<td>5.657</td>
<td>7.944</td>
<td>3.940</td>
<td>4.000</td>
<td>3.972</td>
<td>3.970</td>
<td>7.941</td>
</tr>
</tbody>
</table>

Table 2.1: Lattice Parameter of Samples, calculated by Unit Cell Program

The Unit Cell program\(^3\) was used for calculating lattice parameters. As we expected, all the samples have the orthorhombic arrangement which was first found in GdFeO₃. This structure belongs to space group \(Pbnm\) with \(a \simeq b \simeq \sqrt{2}a_p\) and \(c \simeq 2a_p\) (\(a_p\) being the simple cubic perovskite parameter) and four formula units per unit cell. This structure is described in the standard \(Pnma\) space group. The XRD spectrum could be indexed on a cubic lattice with \(a_c = 2a_p \simeq (7.858 \text{ to } 7.940 \pm 0.002 \text{ Å})\), Table 2.1.

\(^3\) [29]
Chapter 3

Resistivity

3.1 Temperature dependence of resistivity

Measuring the temperature dependence of resistivity reveals important differences between metals, insulators, and semiconductors. Different properties of the material, such as the band gap energy, $E_g$, can be extracted by analyzing resistivity data. Materials can be categorized in three different groups according to their band structure and band gap energy.

3.1.1 Metal

In a metal, there are plenty of charge carriers to carry a current. The factor that determines the resistivity, $\rho$, is their ability to move freely through the material. The factor limiting conductivity is the lattice vibrations which scatter moving electrons; as temperature decreases, these vibrations also decrease. The quantum of energy of a lattice vibration is a Phonon, and there are only certain phonon modes allowed in a crystal. The average number of phonons in a given mode is described by Eq 3.1,

$$< n > = \frac{1}{e^{\hbar \omega/(kT)} - 1}$$  \hspace{1cm} (3.1)

The density of these modes is given by

$$\rho(\omega) = \frac{V \omega^2}{2\pi^2 V_s^3}$$  \hspace{1cm} (3.2)

where $V$ is the volume of the solid and $V_s$ is the speed of sound in the material. The total average number of phonons in the lattice is given by

$$< n_{\text{total}} > = \int_0^{\omega_D} g \rho(\omega) < n > d\omega$$  \hspace{1cm} (3.3)
Figure 3.1: **Schematic diagram of a semiconductor band energy.** In a semiconductor, the band gap is small enough that electrons can be excited from the orbitals in the valence band to the orbitals in the conduction band. This leaves both bands partially filled, and the material can conduct electricity.

where $g$ is the degeneracy factor which is three due to three phonon polarizations and $\omega_D$ is the maximum mode that can be supported by the solid. The Debye temperature is related to the maximum mode frequency $\theta_D=\hbar\omega_D/k$. For $T \ll \theta_D$, $< n_{\text{total}} >$ goes as $T^3$, and for $T \gg \theta_D$, $< n_{\text{total}} >$ goes linearly with $T$. Since more oscillations make it more difficult for an electron to move through a solid, we make resistivity proportional to $< n_{\text{total}} >$.

### 3.1.2 Semiconductor

For a pure semiconductor, phonon vibrations will impede the motion of charge carriers at higher temperatures, but the availability of these charge carriers is the most important factor in determining resistivity. At absolute zero temperature, the valence band in a semiconductor is completely full, Fig. 3.1, and the conduction band is empty. The energy that an electron needs to jump to the conduction band is known as the band gap energy, $E_g$.

\[
n(T) \propto T^{3/2}e^{-\frac{E_g}{2k_BT}}
\]  \hspace{1cm} (3.4)
The relationship between resistivity and temperature for a pure semiconductor is

$$\rho(T) \propto T^{-3/2} e^{E_{g}/kT}$$  \hspace{1cm} (3.5)$$

where the exponential behavior dominates at low temperatures.

### 3.2 Experimental Procedure

#### 3.2.1 Four probe resistivity measurement

The four point probe method was used to determine bulk resistivity. When two contacts are used to measure resistivity, the thermal resistances of the contact points are also measured. Typically the thermal resistance of the point contact for a sample with large resistance is very small thus it can be ignored. However, when one is measuring a very small sample resistance, especially measuring resistance versus temperature, the contact thermal resistance can dominate and completely obscure changes in the resistance of the sample itself. By using four point probe method, the effect of contact thermal resistance can be eliminated.

A schematic of the four point probe is shown in Fig. 3.2. In this diagram four wires have been attached to the sample. A constant current is passed the length of the sample through probes labeled 1 and 4 (Current Probes) in Fig. 3.2. This can be done using a current source or a power supply. If the sample has any resistance to the flow of electrical current, then there will be a voltage drop as the current flows along the sample. The thermal voltage of the contacts is not dependent on the direction of the current. So by switching current polarity and measuring voltage drop, the thermal voltage can be eliminated.

$$V = \frac{V_+ - V_-}{2}$$  \hspace{1cm} (3.6)$$

$$R = \frac{V}{I}$$  \hspace{1cm} (3.7)$$

By knowing the dimensions of the sample, resistivity of the sample can be measured.

$$\rho = \frac{R A}{L}$$  \hspace{1cm} (3.8)$$
3.2.2 Preparation for resistivity measurement

The resistivity measurements were performed on the samples with rectangular shape with dimensions of approximately 2\text{mm} \times 1\text{mm} \times 1\text{mm}. To make good connections between the sample and wires, gold evaporation was used to make four strips of a thin layer of gold on the sample's surface and the wires were connected to these strips with silver paste. A turbo molecular pump was used to make a vacuum up to $10^{-6}$ Torr and a cryostat cooled the samples from room temperature to 14 K. In this study we passed 10 \mu A through the samples.

3.3 Resistivity of $LaV_{1-x}O_3$

All the samples exhibited semiconductor behavior in the whole temperature range studied. Fig. 3.3. The resistivity of the samples was observed to increase when the Vanadium vacancy increased. The Energy gap that was calculated from the resistivity measurements varied from 0.2 eV to 0.3 eV as seen in Fig. [3.4- 3.8]. It should be noted that these energy gaps are about one order of magnitude smaller than the intrinsic Mott-Hubbard gap (1.1 eV) in $LaVO_3$ estimated from optical spectroscopy[7].

Figure 3.2: Schematic diagram of the four probe method
Figure 3.3: Resistivity measurement of $LaV_{1-x}O_3$ with different concentration of Vanadium.
Figure 3.4: Resistivity measurement of $LaVO_3$ and its Energy gap
Figure 3.5: Resistivity measurement of $LaV_{0.98}O_3$ and its Energy gap
Figure 3.6: Resistivity measurement of $LaV_{0.96}O_3$ and its Energy gap
Figure 3.7: Resistivity measurement of $LaV_{0.94}O_3$ and its Energy gap
Figure 3.8: Resistivity measurement of \( \text{LaV}_{0.92}\text{O}_3 \) and its Energy gap
Chapter 3. Resistivity

Figure 3.9: Energy gap versus lattice parameter

The activation energy gap was observed to increase with increasing lattice parameter.

Fig. 3.9, Table 3.1.
Chapter 3. Resistivity

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$E_g \pm 0.0007$ [eV]</th>
<th>$a_c \pm 0.002$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V100</td>
<td>0.226</td>
<td>7.8578</td>
</tr>
<tr>
<td>V98</td>
<td>0.249</td>
<td>7.9094</td>
</tr>
<tr>
<td>V96</td>
<td>0.296</td>
<td>7.9304</td>
</tr>
<tr>
<td>V94</td>
<td>0.288</td>
<td>7.9181</td>
</tr>
<tr>
<td>V92</td>
<td>0.321</td>
<td>7.9414</td>
</tr>
</tbody>
</table>

Table 3.1: Energy gap and lattice parameter of $LaV_{1-x}O_3$
Chapter 4

Magnetization

4.1 Magnetism

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. When a field (H) is applied to a material, it responds by producing a magnetic field which is called magnetization (M). For most materials (M) is proportional to H by Eq. 4.1:

\[ M = \chi H \]  

(4.1)

The proportionality constant, \( \chi \), is the magnetic susceptibility. All materials can be classified into one of five categories depending on their magnetic susceptibility:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism
4. Ferrimagnetism
5. Antiferromagnetism

4.1.1 Diamagnetism

Diamagnetism is a very weak form of magnetism that is only exhibited in the presence of an external magnetic field. Under the influence of an applied field (H) the spining electrons...
Chapter 4. Magnetization

## Diamagnetism

Figure 4.1: Magnetization Versus Magnetic field and Susceptibility Versus Temperature. The susceptibility is negative and temperature independent for diamagnetism.

Precess and this motion, which is a type of electric current, produces a magnetization \( M \) in the opposite direction to that of the applied field (atomic version of Lenz's law). The induced magnetic moment is very small and the direction is opposite in direction to the applied field. The value of susceptibility is independent of temperature. Typically, \( \chi = -1 \times 10^{-6} \text{emu/mol} \).

Figure 4.1 [32, 4]

### 4.1.2 Paramagnetism

Paramagnetism refers to the material having a small and positive susceptibility to magnetic fields. In this class of materials each atom has a magnetic moment due to unpaired electrons which is randomly oriented as a result of thermal fluctuation. The application of a magnetic field creates a slight alignment of these moments and causes a low magnetization in the same direction as the applied field. As the temperature increases, the thermal fluctuation will increase and higher magnetic field is required to align the atomic magnetic moment. As a result of this, susceptibility will decrease with increasing temperature as seen in Fig. 4.2. This
behavior, known as the Curie law, is shown in Eq. 4.2, where C is the Curie Constant. [32, 8, 4]

\[
\chi_p = \frac{C}{T} \tag{4.2}
\]

In fact the Curie law is a special case of the more general Curie-Weiss law (Eq. 4.3):

\[
\chi = \frac{C}{(T - \theta)} \tag{4.3}
\]

\(\theta\) is the Curie Temperature and it is indicative of intermolecular interactions among the magnetic moments.

If \(T > \theta\), Paramagnetic interactions exist.

If \(T < \theta\), ferromagnetic interaction for \(\theta > 0\) and anti-ferromagnetic behavior where \(\theta < 0\).
4.1.3 Ferromagnetic

Ferromagnetic materials have a large and positive susceptibility to an external magnetic field. They exhibit a strong attraction to a magnetic field and are able to retain their magnetic properties after the external field has been removed. Unlike paramagnetic materials, the atomic moments in ferromagnetic materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel alignment of atomic moments—which are called magnetic domains. The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electrons. When a ferromagnetic material is in an unmagnetized state, the domains are nearly randomly organized and the net magnetic field for the part as a whole is zero. When magnetizing force is applied, the domains become aligned to produce a strong magnetic field within the parts. As ferromagnetic materials are heated then alignment of the atomic magnetic moments will be decreased by thermal fluctuation. Eventually the thermal fluctuation becomes so great that the material becomes paramagnetic, the temperature of this transition is the Curie Temperature $\theta$. Above $\theta$ the susceptibility varies according to the Curie-Weiss law. Figure 4.3. [32, 8, 4]

Figure 4.3: Typical behavior of magnetization of ferromagnetic material as function of temperature.
Chapter 4. Magnetization

<table>
<thead>
<tr>
<th>Type of magnetism</th>
<th>Susceptibility</th>
<th>Magnetic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>Small and negative</td>
<td>No magnetic moment</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>Small and positive</td>
<td>Randomly oriented magnetic moments</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>Large and Positive</td>
<td>Parallel aligned magnetic moments</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>large and positive</td>
<td>Anti-parallel aligned magnetic moments</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>Small and positive</td>
<td>Parallel and anti-parallel aligned magnetic moments</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of different magnetic materials.

4.1.4 Ferrimagnetism

Ferrimagnetism is only observed in compounds, which have more complex crystal structures than pure elements. Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others. The material breaks down into magnetic domains, just like a ferromagnetic material and the magnetic behavior is also very similar, although ferrimagnetic materials usually have lower saturation magnetization. [4]

4.1.5 Antiferromagnetism

Antiferromagnetic materials are very similar to ferromagnetic materials but the exchange interaction between neighboring atoms leads to the anti-parallel alignment of the atomic magnetic moments. The clue to antiferromagnetism is the behavior of the susceptibility above a critical temperature, called the Néel Temperature ($T_N$). Above $T_N$, the susceptibility obeys the Curie-Weiss law for paramagnets but with a negative intercept indicating negative exchange interactions. [32, 8, 4]
Figure 4.4: **Type of magnetism:** (A) Paramagnetism (B) Ferromagnetism (C) Antiferromagnetism (D) Ferrimagnetism. [3]

## 4.2 Experimental procedure

### 4.2.1 SQUID

The SQUID (Superconducting QUantum Interference Device) which was invented in 1962 when B.D Josephson\(^1\) developed the Josephson junction is one of the most sensitive instruments for magnetometry measurements. It uses a combination of superconducting materials and Josephson junctions to measure magnetic fields with resolutions up to \(\sim 10^{-14}\) kG or greater. [5]

**Electron-pair Waves**

In superconductors electron pairs are charge carriers, known as Cooper Pairs. The electron-electron coupling is weak and can be destroyed by thermal motion of the lattice. For this reason superconductivity exists only at low temperatures. The Cooper pairs do not have spin 1/2 and therefore do not follow Pauli’s principle (1 electron per state). A large number of Cooper pairs can populate one collective state. This state is stable and requires some

---

additional energy input (thermal energy) to be destroyed. The binding energy of Cooper pairs in the collective state is several meV. The formation of the collective state of Cooper pairs takes place at $T < T_c$. Each pair can be represented by a wavefunction of the form Eq. 4.4 [5]

$$\Phi_P = \Phi e^{i(P,r)/\hbar}$$

(4.4)

where $P$ is the net momentum of the pair whose center of mass is at $r$. In a uniform current density all the electron wavelengths will be equal with the superposition of these coherent waves producing a single wave of the same wavelength, meaning all of the electron-pairs in a superconductor can be described by a single wavefunction Eq. 4.5

$$\Psi_P = \Psi e^{i(P,r)/\hbar}$$

(4.5)

This electron-pair wave retains its phase coherence over long distances and it is this characteristic which leads to interference and diffraction phenomena. As they are macroscopic manifestations of quantum interactions the phenomena are collectively termed "Quantum Interference".

**Josephson Tunnelling**

If two superconducting regions are kept totally isolated from each other the phases of the electron-pairs in the two regions will be unrelated. If the two regions are brought together then as they come close electron-pairs will be able to tunnel across the gap and the two electron-pair waves will become coupled. As the separation decreases the strength of the coupling increases. The tunneling of the electron-pairs across the gap carries with it a superconducting current as predicted by B.D. Josephson [19] and is called “Josephson Tunnelling” with the junction between the two superconductors called a “Josephson Junction”.

Like a superconductor this gap has a critical current. If a supercurrent, $i_s$, flows across a gap between regions with a phase difference, $\Delta \phi$, it is related to the critical current, $i_c$, by
Chapter 4. Magnetization

Eq. 4.6

\[ i_s = i_c \sin \Delta \phi \]  \hspace{1cm} (4.6)

so that the maximum current flows across the gap when there is a phase difference of \( \pi/2 \), where \( i_s = i_c \).

The Josephson Tunneling Junction is a special case of a more general type of weak link between two superconductors. Other forms include constrictions and point contacts but the general form is of a region between two superconductors which has a much lower critical current and through which a magnetic field can penetrate. [5]

SQUID

In the original form, the SQUID consists of two Josephson tunnelled junctions connected in parallel on a superconducting loop. Figure 4.5. The total current \( I = I_1 + I_2 \) is a periodic function of the flux through the ring.

\[ I_{total} = 2 \ast J_0 \ast \sin(\delta_0) \ast \cos(2\pi e\phi/h) \]  \hspace{1cm} (4.7)

The current varies with \( \phi \) and has maxima when

\[ (2\pi e/h)\phi = n\pi \]  \hspace{1cm} (4.8)

where \( n \) is an integer. The quantity \( \Phi_0 = h/(2e) \) is called the flux quantum. A change in the magnetic field will cause a change in the flux through the SQUID, by counting the number of oscillations \( N \) the overall change in flux can be calculated by Eq. 4.9:

\[ \phi_{total} = N \ast \Phi_0 \]  \hspace{1cm} (4.9)

There are two main kinds of SQUIDs; DC and RF SQUIDS. The DC SQUIDs usually have two or more Josephson junctions. This makes them more sensitive but difficult and expensive to produce. The RF SQUIDs consist of a single junction interrupting a superconducting loop. Figure 4.6 shows schematically how a SQUID responds for a dipole and also it shows the movement of the sample within the SQUID pickup coils.
Figure 4.5: Superconducting quantum interference device as a simple magnetometer

Figure 4.6: SQUID SCHEMA. This picture shows the ideal SQUID response for a dipole and also shows the movement of the sample within the SQUID pickup coils. [5]
4.2.2 DC Magnetometry

DC magnetic measurements determine the equilibrium value of the magnetization in a sample. The sample is magnetized by a constant magnetic field and the magnetic moment of the sample is measured, producing a DC magnetization curve $M(H)$. The moment is measured by force, torque or induction techniques, the last being the most common in modern instruments. Inductive measurements are performed by moving the sample relative to a set of pickup coils, either by vibration or one-shot extraction. In conventional inductive magnetometers, one measures the voltage induced by the moving magnetic moment of the sample in a set of copper pickup coils. A much more sensitive technique uses a set of superconducting pickup coils and a SQUID to measure the current induced in superconducting pickup coils, yielding high sensitivity that is independent of sample speed during extraction. Inductive magnetometers can also be used to perform AC magnetic measurements. [26]
4.2.3 AC Magnetometry

In AC magnetic measurements, a small AC drive magnetic field is superimposed on the DC field, causing a time-dependent moment in the sample. The field of the time-dependent moment induces a current in the pickup coils, allowing measurement without sample motion. The detection circuitry is configured to detect only in a narrow frequency band, normally at the fundamental frequency (that of the AC drive field). [26]

4.3 Magnetization of ceramic sample $LaV_{1-x}O_3$

The magnetic susceptibility of $LaV_{1-x}O_3$ Fig. 4.8 with different Vanadium concentration exhibited a peak at 140 K, indicative of antiferromagnetic ordering. In general, the observed susceptibility $\chi(T)$ is written as the sum of spin, orbital and core-diamagnetic contributions as Eq. 4.10 [21];

$$\chi(T) = \chi_{\text{spin}}(T) + \chi_{\text{VV}} + \chi_{\text{core}}$$  \hspace{1cm} (4.10)

Here $\chi_{\text{spin}}(T)$ is the d-spin susceptibility, $\chi_{\text{VV}}$ is the Van Vleck orbital susceptibility and $\chi_{\text{core}}$ is the diamagnetic susceptibility of inner-core electrons. $\chi_{\text{VV}}$ and $\chi_{\text{core}}$ are generally considered to be T independent. The Curie-Weiss fit to the data above $T_N$ yields a negative paramagnetic Curie temperature indicative of an antiferromagnetic interaction Fig. 4.9. Table 4.2 lists the Néel temperature $T_N$, the paramagnetic Curie temperature $\theta$ and molar Curie constant $C_M$, for $LaV_{1-x}O_3$ as obtained by this work and other workers. For finding these values, we use $\chi_{\text{core}} = -0.66 \times 10^{-4} \text{cm}^3/\text{mol}$ [23] and $\chi_{\text{VV}} = 2.1 \times 10^{-4} \text{cm}^3/\text{mol}$ (same as in $V_2O_3$, which has trivalent vanadium [18]). In light of the uncertainty in determining the temperature-independent terms in the susceptibility, the values obtained for $\theta$ perhaps might not be very meaningful. Our value of $T_N$ is close to that obtained by Zubkov et al.\textsuperscript{2} from neutron diffraction.

\textsuperscript{2}[34]
Figure 4.8: Susceptibility Versus Temperature. The magnetic susceptibility of all $LaV_{1-x}O_3$ with different Vanadium concentrations exhibit a peak at $\sim 140K$, indicative of antiferromagnetic ordering.
Chapter 4. Magnetization

Figure 4.9: Inverse of Susceptibility Versus Temperature. Curie-Weiss fits to the data above $T_N$ yield negative paramagnetic Curie temperatures indicative of antiferromagnetic ordering for all the samples.
Table 4.2: Values of the Néel temperature $T_N$, the paramagnetic Curie temperature $\theta$ and molar Curie constant $C_M$, for $LaV_{1-x}O_3$ as obtained by this work and other workers.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_N$ [K]</th>
<th>$\theta$ [K]</th>
<th>$C_M$ [$cm^3Kmol^{-1}]$</th>
<th>$\mu_{eff}$ ($\mu_B$)</th>
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<td>$LaVO_3$</td>
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<td>1.55</td>
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<td>3.62</td>
</tr>
</tbody>
</table>
Chapter 5

Conclusions

Room temperature powder X-ray diffraction data showed all the $LaV_{1-x}O_3$ perovskites were orthorhombic belongs to space group $Pbnm$ which is isostructural with $GdFeO_3$. The lattice parameters are listed in Table 2.1. It's reported by other workers that there is a structure transition from orthorhombically-distorted perovskite structure with space group Pnma to monoclinic structure with space group $P2_1/a$. The lattice parameters increase with increasing Vanadium vacancy.

All the samples show semiconductor behavior in the whole temperature range studied. Resistivity of the samples increase with increase in Vanadium vacancy. The energy gap calculated from resistivity measurements varies from 0.2 eV to 0.3 eV. It is to be noted here that these energy gaps are about one order of magnitude smaller than intrinsic Mott-Hubbard gap(1.1 eV) in $LaVO_3$ estimated from optical spectroscopy[4]. We believe that the smaller energy gap arises due to the excitation to the localized doped holes states above the valence band, and we call this energy gap the activation energy. The activation energy gaps increase with increase in lattice parameters.

The susceptibilities exhibit maxima at $T_N \sim 140$ K and exhibit Curie-Weiss Like decrease above $T_N$. There is no observable change in the positions of the peaks regarding the amount of vacancy in Vanadium. The T dependence of $\chi$ below $T_N$ looks like the one in usual antiferromagnets.
Bibliography


