Structural, electronic, and magnetic properties of La$_x$Sr$_{1-x}$VO$_3$ ($0 \leq x \leq 1.0$)

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Structural, electronic, and magnetic properties of $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ ($0 \leq x \leq 1.0$)

Mahajan, Avinash Vithal, Ph.D.
Iowa State University, 1991
Structural, electronic, and magnetic properties of 
$\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ ($0 \leq x \leq 1.0$)

by

Avinash Vithal Mahajan

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For the Major Department
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For the Graduate College

Iowa State University 
Ames, Iowa  
1991
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CHAPTER 1. INTRODUCTION

The Metal-insulator Transition

Traditionally, metal-insulator transitions have been divided into two categories. In the first case, atomic site disorder dominates and the carriers are localized due to Anderson localization [1]. In such a situation, the atomic potential is no longer periodic and the electrons can no longer be represented by Bloch waves and therefore are localized in space. They can move from one lattice site to another by thermally activated hopping. The logarithm of the conductivity, at low temperatures, is proportional to \( T^{1/(1+d)} \) (\( d \) is the dimensionality of the system) and the phenomenon is known as variable range hopping.

The transition metal monoxides, such as NiO, are among the most widely studied class of insulators known as Mott insulators. In crystalline materials, where atomic site disorder is minimal and the atomic potential is periodic, it is favourable for an electron to lower its kinetic energy by hopping from atom to atom. As a result the electrons tend to form a band and hence be itinerant. Since hopping of electrons between atoms will be opposed by the Coulomb repulsion between the electrons, it was proposed by Mott [2] that when these electron-electron correlations became strong, a metal-insulator transition would occur since it would be energetically more favourable for the electrons to remain localized. The effects of correlation were treated
by Hubbard within the Hubbard model [3, 4] and he found that for large correlation
the electronic band is split into two sub-bands (often referred to as the lower and the
upper Hubbard bands) separated by an energy gap, giving rise to insulating behavior
observed in compounds such as NiO.

The Perovskite Structure

The perovskites form a family of compounds having a crystal structure similar
to that of the mineral perovskite CaTiO$_3$ (see Figure 1.1 for the cubic perovskite
structure). The perovskite structure can be thought of as the $n = \infty$ member of the
family of compounds known as Ruddlesdon-Popper phases [5, 6], with the general
formula $A_{n+1}B_nX_{3n+1}$, first observed in the Sr-Ti-O system.

As seen in Figure 1.1 the basic building blocks for the perovskite structure are
the BO$_6$ octahedra, where B is a cation. Stoichiometric SrTiO$_3$ is an insulator and
on doping (SrTiO$_3$$_{1-x}$) undergoes a metal-insulator transition and was in fact the
first ternary oxide to be found superconducting ($T_c$ (max) = 0.7 K) [7]. $A_xWO_3$
($T_c$ (max) = 6 K) [8], $A_xMoO_3$ ($T_c$ (max) = 4 K) [9], $A_xReO_3$ ($T_c$ (max) = 4 K)
[9], BaPb$_{1-x}$Bi$_x$O$_3$ ($T_c$ (max) = 13 K) [10] and Ba$_{1-x}$K$_x$BiO$_3$ ($T_c$ (max) = 29
K) [11] are further examples of compounds in the perovskite family which exhibit
superconductivity. Li$_{1+x}$Ti$_{2-x}$O$_4$ has the spinel structure, with TiO$_6$ octahedra
as building blocks, and exhibits superconductivity ($T_c$ (max) = 13 K) [12]. Not to
be forgotten are the high $T_c$ superconductors (La$_{2-x}$Sr$_x$CuO$_4$, YBa$_2Cu$_3$_O_7$, etc.)
which too possess structures based on perovskite building blocks. The vicinity of these
superconductors, many of which have high $T_c$s, to a composition induced metal to
insulator transition is to be noted.
Figure 1.1: The cubic Perovskite structure
In view of the absence of a consensus regarding the governing mechanism(s) responsible for the high superconducting transition temperatures in the copper based compounds such as La$_2-x$Sr$_x$CuO$_4$, it appears that investigations on systems similar to the cuprate family of superconductors is warranted. This would perhaps, help identify the role (or lack thereof) of the various characteristic features (such as dimensionality, spin fluctuations, closeness to the metal-insulator boundary, etc.) in relation to superconductivity.

**The La$_x$Sr$_{1-x}$VO$_3$ System**

SrVO$_3$ may be considered as an electron analog of La$_2$CuO$_4$. In La$_2$CuO$_4$, copper has the d$^9$ electron configuration which implies one hole per formula unit. SrVO$_3$ has one electron per formula unit. The system La$_x$Sr$_{1-x}$VO$_3$ (0 ≤ x ≤ 1) is of interest because of its striking similarities to the high-$T_c$ superconductors discovered in the recent past [13, 14]. The aforementioned system has a three-dimensional perovskite structure. It exhibits a composition-induced Pauli paramagnet to antiferromagnetic insulator transition with increasing x, at x = 0.8 [15, 16, 17, 18]. These features are reminiscent of the properties of high-$T_c$ superconductors. In La$_2-x$Sr$_x$CuO$_4$, YBa$_2$Cu$_3$O$_{6+x}$ and Bi$_2$Sr$_2$Ca$_x$Y$_{1-x}$Cu$_2$O$_8$ for instance, the systems undergo antiferromagnetic insulator to superconducting metal transition with increasing x [19, 20, 21]. Furthermore, in a narrow range of composition (0.1 < x < 0.3), La$_2-x$Sr$_x$CuO$_4$ becomes superconducting at low temperatures, while for x ≥ 0.3 the system behaves more like a d-band normal metal [22]. Thus the change from La$_2$CuO$_4$ to the heavily Sr doped metallic phase apparently spans a region from the limit of strong correlation (i.e., local moments) to the limit corresponding
to conventional band theory. The superconducting range falls into the theoretically difficult regime of competing electron correlation and transfer effects.

The La$_x$Sr$_{1-x}$VO$_3$ system was first investigated by Reuter and Wollnik [23]. Under the conditions employed in their study, they found that the single phase region was $0.5 \leq x \leq 1$. Dougier and Casalot [15] found the single phase region to be $0.6 \leq x \leq 1.0$, with the structure being a hexagonal distortion of the cubic perovskite for $x \geq 0.8$. Dougier and Hagenmuller [16] concluded from their study that the structure was tetragonal for $0.9 \leq x \leq 1.0$, orthorhombic for $0.77 < x < 0.9$ and hexagonal for $0.6 \leq x \leq 0.77$. They found the single phase region to be $0.6 \leq x \leq 1.0$. On the other hand, Shin-ike et al. [18] found a continuous solid solution from $x = 0$ to $x = 1$ with a cubic to tetragonal transition occurring with increasing $x$ at $x \approx 0.8$. SrVO$_3$ has a cubic perovskite structure [23, 24, 25, 26]. The compound LaVO$_3$ has been reported to be a cubic perovskite [27] with $a_0 = 3.91$ Å, a cubic perovskite with $a_0 = 7.842$ Å[28], a tetragonal distortion of the cubic perovskite [24, 29, 30, 31, 32], and a hexagonal distortion of the cubic perovskite structure [15]. The compound undergoes a tetragonal ($c/a\sqrt{2} > 1$) to orthorhombic ($c/a\sqrt{2} < 1$) structural phase transition with decreasing temperature in the vicinity of 130 K [31, 33, 34].

Four-probe electrical resistivity measurements on a single crystal of LaVO$_3$ show activated conduction with an activation energy of 0.14 eV. Resistivity data on single crystal SrVO$_3$ [25, 26] show metallic behaviour. Dougier and Casalot [15] concluded from their study that a metal-insulator transition occurred with increasing $x$ at $x \approx 0.8$ and that the activation energy (from resistivity measurements) for the insulating samples increased monotonically with $x$. It has been suggested [38] that La$^{3+}$/Sr$^{2+}$ atomic site disorder induces Anderson localization [1] and is the cause of the metal-
insulator transition. For a system exhibiting a metal-insulator transition, due to
Anderson localization of carriers, the activation energy on the insulating side of the
transition should vary as $\epsilon \propto (x-x_0)^{1.8}$ [35] where $x_0$ is the value of $x$ at which
the metal to insulator transition takes place. According to the work of Sayer et al. [17]
and Dougier et al. [16] the value of the exponent was found to be $1.8\pm0.5$ and $x_0 = 0.75$.
However, other models lead to a value (of the exponent) of 1.6 [36] and are
equally likely.

Another prediction of the Anderson model is a temperature dependent conduc­
tivity which varies with temperature as $\ln \sigma \propto T^{1/4}$ at low temperatures, signifying
the onset of variable range hopping. However, even in systems where electron cor­
relations play a dominant role (such as La$_{2-x}$Sr$_x$CuO$_4$) variable range hopping has
been observed at low temperatures [39] due to the (minor) role played by atomic site
disorder. Sayer et al. [17] observed a $\ln \sigma \propto T^{1/4}$ behavior at low temperatures (for
semiconducting samples in the La$_x$Sr$_{1-x}$VO$_3$ system), signifying the onset of vari­
able range hopping. It is also expected that a frequency dependent ac conductivity
be observed in the hopping regime. However, the temperatures below which variable
range hopping is observed (in the case of La$_x$Sr$_{1-x}$VO$_3$) are not consistent with the
temperatures below which a frequency dependent ac conductivity [17] is observed.
Also, a predicted power law dependence $\sigma \propto \omega^{0.8}$ is not observed and the observed
exponent is approximately 0.5 [17].

The thermopower data for the La$_x$Sr$_{1-x}$VO$_3$ are ambiguous. Dougier and Ha­
genmuller [16] find that for $x = 0.95$ and 0.9 the thermopower ($S$) has a temperature
dependence characteristic of transport due to carriers at a mobility edge ($S \propto 1/T$)
down to 77 K and does not show a transition to a hopping dominated behaviour
(S $\propto$ T) expected at low temperatures (even though the conductivity does), in the temperature range studied. On the other hand, for $x = 0.85$ and $0.8$ the temperature dependence is that expected for hopping (although the conductivity does not show this behavior) but does not change over to the behaviour expected for transport due to carriers at a mobility edge at higher temperatures in the temperature range studied, 77 K to 300 K. For the only metallic composition measured, $x = 0.725$, the thermopower is negative. This would indicate the sign of the charge carriers to be negative but doping LaVO$_3$ by Sr is equivalent to hole doping (S is positive for the semiconducting compositions). Measurements by other researchers [17, 41] are in agreement with these results. Prasad et al. [42] were unable to detect a Hall voltage (for La$_x$Sr$_{1-x}$VO$_3$, $0.6 \leq x \leq 1$) under the conditions employed in their experiment.

Magnetic susceptibility measurements by Dougier and Hagenmuller [16] show that samples with $x \geq 0.8$ order antiferromagnetically. In the case of LaVO$_3$ the magnetic susceptibility exhibits a peak near 140 K and a Curie-Weiss fit to the data above $T_N$, yields a negative paramagnetic Curie temperature indicative of antiferromagnetic V-V interactions [16, 29, 31, 32, 33, 40]. The saturation moment at 4.2 K, as obtained from neutron diffraction investigation [29, 34], was found to be $1.3 \pm 0.1 \mu_B$ which is much less than the spin-only moment ($gS\mu_B \approx 2 \mu_B$) expected for a $S = 1$ system such as V$^{3+}$ with $g = 2$. Dougier and Hagenmuller [31] found that LaVO$_3$ exhibited weak ferromagnetism below the Néel temperature.

High resolution electron spectroscopy measurements on these compounds [13] show that in all the insulating samples the density of states at the Fermi level is zero and that there is one filled d-band. This contradicts the view of Mott et al. [38] that the lower and upper Hubbard bands overlap in the insulating samples and that the
states at the Fermi level are localized due to Anderson localization. The width of the d-band was found to increase as one goes from the insulator to the metal.

Herein, we present the combined results of magnetic susceptibility and $^{51}$V NMR measurements which were carried out to elucidate the nature of the metal to insulator transition and of the electronic character of the metallic phase particularly regarding the importance of electron correlations to the metal-insulator transition. With our preparation techniques, a continuous range of solid solution exists for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ from $x = 0$ to $x = 1$. We find that the metal-insulator transition in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ results from electron correlations, with La-Sr atomic site disorder playing a minor role. In this respect the comparison with high-$T_c$ Cu-based oxide systems turns out to be quite enlightening. In particular, we find no evidence for antiferromagnetic correlations in the metallic state ($x \leq 0.7$) of $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$, in strong contrast to, e.g., $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, where clear evidence of these correlations in the metallic state is found [44, 45]. Further, anomalous diamagnetism was observed in $\text{LaVO}_3$ below $T_N \approx 135$ K, under certain conditions related to the magnetic field and thermal history of the sample. This diamagnetism appears to be related to ferrimagnetism which arises from magnetically inequivalent $\text{V}^{3+}$ ions.
CHAPTER 2. EXPERIMENTAL DETAILS

Sample Preparation

The starting materials were pre-dried La$_2$O$_3$ (99.99%), pre-dried SrCO$_3$ (99.99 %), and V$_2$O$_3$ (95+ %). Pellets of La$_2$O$_3$ + SrCO$_3$ were prereacted in air at 930 °C until the appropriate weight loss (corresponding to the loss of CO$_2$) was obtained. V$_2$O$_3$ was added to this precursor and pellets of the ground mixture (wrapped in platinum foils and placed in an alumina boat) were reacted in a tantalum tube furnace at 1500 °C under a vacuum of 10$^{-4}$ Torr. Samples were reground, repelletized and refired until single phase products were obtained. Generally 2 to 3 firings were sufficient to give single phase products (Set 1). Another set of samples was prepared by arc melting the mixtures of prereacted La$_2$O$_3$ and SrCO$_3$ with V$_2$O$_3$, in an arc furnace on a water cooled copper hearth. This procedure also gave single phase products (Set 2). LaVO$_3$ was prepared, for both sets, by arc melting the pelletized mixtures of La$_2$O$_3$ and V$_2$O$_3$. In the first two sets of samples it was realized, on making magnetic measurements, that the samples contained about 0.1-0.2% ferromagnetic impurities due to the low purity of the V$_2$O$_3$ starting material. This made it necessary to employ a sizeable correction to the measured magnetic susceptibility. In order to remove any ambiguity regarding the interpretation of magnetic susceptibility data, we prepared a third set of samples (Set 3) in which we employed the
use of 99.9% pure V$_2$O$_3$. This set was prepared by the same method as in Set 1. This led to the formation of single phase samples which had less than 15 ppm of ferromagnetic impurities as deduced from magnetization measurements.

**Sample Characterization**

X-ray powder diffraction analysis was done on a Rigaku Geigerflex diffractometer, with a curved crystal graphite monochromator, using Cu Kα radiation (λ = 1.5418 Å). The peak positions were corrected for zero point shift and nonlinearity using Si or Al$_2$O$_3$ as an internal standard. Lattice parameters were obtained using a least squares fitting procedure. Low temperature (20 K < T < 300 K) x-ray diffraction was performed on two samples in Set 2 (x = 0.9, 1.0) using a closed cycle helium refrigerator.

Thermogravimetric analysis was done on the samples to determine their oxygen content using a Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA). The vanadium oxidation state was determined by noting the weight gain in the TGA on heating the sample to 1000 °C in pure oxygen and assuming that the product contained only V$^{+5}$.

D. C. susceptibility measurements between 4 K and 400 K were performed using a commercial (Quantum Design) SQUID magnetometer. Contributions due to ferromagnetic impurities were subtracted by extracting the saturation magnetization, from isotherms of magnetization versus the applied field (M(H)). This was done by fitting to a straight line, the data in the field region where ferromagnetic impurities had saturated and magnetization varied linearly with the applied field. The intercept of this linear fit on the y axis gives us the saturation magnetization of the
ferromagnetic impurity at the temperature at which the isotherm was measured (see Figure 2.1 for an example). This was then subtracted from the measured magnetic moment. The isotherms were measured at temperatures of 5 K, 50 K, 100 K, 200 K, 300 K and 400 K. Linear interpolation of the available data was performed in order to get the ferromagnetic impurity contribution at intermediate temperatures. D.C. resistance measurements were done using a standard 4-probe method.

$^{51}$V NMR measurements were performed both with a phase-coherent pulsed spectrometer in a magnetic field of 82 kGauss and with a modified Varian continuous wave (CW) spectrometer in a field of about 10 kGauss. For the pulsed measurements, the NMR spectrometer employed a programmable pulse sequencer [46], a double sideband r.f. switch [47] and an NMR receiver following the design of Adduci et al. [48]. An Oxford Instruments superconducting magnet with variable temperature control was used. For the CW measurements we used a Torgeson spectrometer [49] and Varian probe and electromagnet. Care was taken to keep the amplitude of the modulating field (in the case of CW measurements) less than $\approx$ one-fifth of the line width of the sample under study, in order to eliminate any artificial broadening. The magnetic field was calibrated with an aqueous solution of AlCl$_3$ for the superconducting magnet as well as for the electromagnet used for CW measurements. For the electromagnet, the field calibration was checked before and after every run. The stability of the electromagnet was found to be within about half a Gauss over a period of several days.

The NMR spectrum in 82 kGauss was obtained both from the Fourier transform (FT) of the free induction decay (FID) and from the FT of half of the spin echo signal following a $\pi/2 - \pi$ pulse sequence. For the insulating paramagnetic samples
Figure 2.1: Magnetization $M$ versus the applied field $H$ at 50 K for $La_{0.3}Sr_{0.7}VO_3$ (Set 3). The solid line is a fit to the data between 5 kGauss and 20 kGauss.
(x > 0.7), the homogeneous line width at half intensity $\delta \omega$ becomes as large as $350 \times 10^3$ rad/s corresponding to a transverse relaxation time $T_2 = 2 \times (\delta \omega)^{-1} \approx 6 \mu s$. Under these conditions the NMR spectrum cannot be detected by pulse FT NMR and only CW measurements can be performed. It should be noted that in this limiting case one is close to the condition $T_1^{-1} = T_2^{-1}$ and thus the measurement of the homogeneous linewidth yields an estimate of both $T_2$ and $T_1$ [65].

The $^{51}$V nucleus has $I = 7/2$, $\gamma = 11.193$ MHz/T and $Q = -0.05 \times 10^{-21}$ cm$^2$. Due to the small value of the quadrupole moment $Q$ and of the Sternheimer anti-shielding factor ($1 - \gamma \infty$) the quadrupole effects on the $^{51}$V NMR spectrum are found to be, in general, only first order even in non-cubic materials [50]. The $^{51}$V NMR spectra in the 82 kGauss magnetic field are shown in Chapter 3 for different samples. It is seen that the line broadens dramatically upon increasing the La content. For $x = 0.7$, the line width is larger than the spectral width of the radio frequency pulse and therefore the line profile was obtained by plotting the height of the echo signal as a function of the transmitter frequency. For the $x = 0.6$ (Set 2) sample, pulse measurements performed at a lower field ($H = 2$ T), indicate that the broadening decreases linearly with decreasing magnetic field as expected for inhomogeneous magnetic broadening although a small broad component of the line, about 100 kHz wide, remains present even in low fields (see Figure 2.2). This wide second component is probably due to first order satellite distribution due to the non-uniform electric field gradients experienced by the $^{51}$V nuclei and due to the random distribution of La$^{3+}$ and Sr$^{2+}$ ions and/or a deviation from cubic symmetry.

For $x < 0.5$, the NMR spectrum is narrower than the spectral width of the radio frequency pulse ($\sim 60$ kHz) and the spin-lattice relaxation rate was measured
Figure 2.2: NMR spectra for La$_{0.6}$Sr$_{0.4}$VO$_3$ (Set 2) in two fields, showing that a 100 kHz component to the line width is present at low fields also
either by monitoring the exponential recovery of the nuclear magnetization after a saturating $\pi/2$ pulse or a single $\pi$ pulse. For $x \geq 0.5$ the inhomogeneous broadening prevents the complete saturation of the NMR line even with a long sequence of $\pi/2$ pulses. However, the recovery was found to be exponential after an initial fast recovery of the nuclear magnetization by about 50% due to incomplete saturation. This implies that, due to the fact that $T_2 \ll T_1$, the nuclear Zeeman levels achieve a common spin temperature after a very short time compared to $T_1$. Thus we can safely assume that even for the samples with $x \geq 0.5$, the measured $T_{1}^{-1} = 2W_M$, with $W_M$ the magnetic relaxation transition probability [51], although a larger systematic error is present in this case.

For the case of the antiferromagnetic insulator LaVO$_3$, the resonance line width was measured as a function of temperature. A heater was used in combination with cold gas (obtained from boiling off liquid nitrogen in a dewar) in order to attain low temperatures.
CHAPTER 3. RESULTS AND DISCUSSION

X-ray Diffraction, TGA, and Resistance Measurements

Contrary to some reports [15, 23, 24] and in agreement with the results of Shin-ike et al. [18] we find from x-ray powder diffraction analysis that the \( \text{La}_{x}\text{Sr}_{1-x}\text{VO}_3 \) system exhibits complete solid solubility from \( x = 0 \) to \( x = 1 \). Different preparation conditions in the different investigations may be responsible for this discrepancy.

The pseudocubic lattice parameters, \( a_0 \sim 3.9 \) Å, obtained from our measurements are listed in Tables 3.1, 3.2, and 3.3. They are plotted versus composition \( x \) in Figure 3.1, along with the results of Shin-ike et al. [18]. The differences between our data and those of Shin-ike et al. may be due to the different preparation conditions and differing oxygen contents in the samples (see, e.g., the three samples with \( x = 0.4 \) in Figure 3.1). Note that if \( a_c \) is the lattice parameter of the cubic unit cell then for the tetragonal unit cell \( a_t = a_c \sqrt{2} = b_t \) and \( c_t = 2a_c \) and for the orthorhombic unit cell \( a_o \) and \( b_o \) are slightly different from \( a_c \sqrt{2} \) and \( c_o \approx 2a_c \).

The x-ray patterns of compounds with \( x \geq 0.7 \), in all the three sets, could be indexed based on a tetragonal distortion of the cubic perovskite structure. For \( x < 0.7 \), (most) samples were found to be cubic. Some samples, for \( x < 0.7 \), had tetragonal/orthorhombic distortions from cubic symmetry which was evidenced by the presence of additional peaks. Figure 3.2 shows the x-ray diffraction patterns for
Table 3.1: Variation of the weight gain on oxidation \( w \), Oxygen content \( 3 + \delta \), effective La doping \( x^* \), pseudocubic lattice parameter \( a_0 \) (± 0.001 Å) and the Curie constant (from a low temperature Curie term presumably due to isolated magnetic defects) with \( x \) in \( \text{La}_x\text{Sr}_{1-x}\text{VO}_{3+\delta} \) (Set 1)

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<th>( w ) (%)</th>
<th>( 3 + \delta )</th>
<th>( x^* )</th>
<th>( a_0 ) (Å)</th>
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Table 3.2: Variation of the weight gain on oxidation $w$, Oxygen content $3 + \delta$, effective La doping $x^*$, pseudocubic lattice parameter $a_0$ (± 0.001 Å) and the Curie constant (from a low temperature Curie term presumably due to isolated magnetic defects) with $x$ in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3+\delta$ (Set 2)

<table>
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<tr>
<th>$x$</th>
<th>$w$ (%)</th>
<th>$3 + \delta$</th>
<th>$x^*$</th>
<th>$a_0$ (Å)</th>
<th>$C \times 10^{-3}$ cm$^3$K/mole V</th>
</tr>
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<tbody>
<tr>
<td>0.1</td>
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<td>2.926</td>
<td>0.248</td>
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</tr>
<tr>
<td>0.2</td>
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<td>2.991</td>
<td>0.218</td>
<td>3.847</td>
<td>3.9</td>
</tr>
<tr>
<td>0.3</td>
<td>5.509</td>
<td>2.957</td>
<td>0.386</td>
<td>3.860</td>
<td>0.9</td>
</tr>
<tr>
<td>0.4</td>
<td>5.419</td>
<td>2.999</td>
<td>0.403</td>
<td>3.869</td>
<td>3.7</td>
</tr>
<tr>
<td>0.5</td>
<td>6.114</td>
<td>2.943</td>
<td>0.615</td>
<td>3.887</td>
<td>1.8</td>
</tr>
<tr>
<td>0.6</td>
<td>6.118</td>
<td>2.971</td>
<td>0.659</td>
<td>3.893</td>
<td>1.6</td>
</tr>
<tr>
<td>0.7</td>
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<td>3.018</td>
<td>0.665</td>
<td>3.894</td>
<td>7.4</td>
</tr>
<tr>
<td>0.8</td>
<td>6.069</td>
<td>3.035</td>
<td>0.731</td>
<td>3.904</td>
<td>1.0</td>
</tr>
<tr>
<td>0.9</td>
<td>6.300</td>
<td>3.032</td>
<td>0.837</td>
<td>3.915</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>6.291</td>
<td>3.061</td>
<td>0.878</td>
<td>3.925</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.3: Variation of the weight gain on oxidation w, Oxygen content $3 + \delta$, effective La doping $x^*$, pseudocubic lattice parameter $a_0$ ($\pm 0.004 \, \text{Å}$) and the Curie constant (from a low temperature Curie term presumably due to isolated magnetic defects) with $x$ in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3+\delta$ (Set 3)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$w$ (%)</th>
<th>$3 + \delta$</th>
<th>$x^*$</th>
<th>$a_0$ (Å)</th>
<th>$C \times 10^{-3}$ cm$^3$K/mole V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.734</td>
<td>2.984</td>
<td>0.133</td>
<td>3.847</td>
<td>0.79</td>
</tr>
<tr>
<td>0.3</td>
<td>4.948</td>
<td>3.024</td>
<td>0.252</td>
<td>3.864</td>
<td>0.74</td>
</tr>
<tr>
<td>0.4</td>
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<td>0.370</td>
<td>3.865</td>
<td>0.92</td>
</tr>
<tr>
<td>0.5</td>
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<td>3.046</td>
<td>0.408</td>
<td>3.872</td>
<td>1.12</td>
</tr>
<tr>
<td>0.6</td>
<td>5.697</td>
<td>3.025</td>
<td>0.550</td>
<td>3.879</td>
<td>0.82</td>
</tr>
<tr>
<td>0.7</td>
<td>5.992</td>
<td>3.016</td>
<td>0.668</td>
<td>3.895</td>
<td>0.91</td>
</tr>
<tr>
<td>0.8</td>
<td>6.102</td>
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<td>0.740</td>
<td>3.898</td>
<td>1.86</td>
</tr>
<tr>
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<td>0.798</td>
<td>3.918</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>6.583</td>
<td>3.020</td>
<td>0.960</td>
<td>3.928</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.1: Variation of the cubic or the pseudocubic lattice parameter $a_0$ (±0.004 Å) with La doping $x$ for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$. 
Figure 3.2: X-ray pattern of intensity I versus 2θ for x = 0.6, for Set 2 and Set 3, where arrows indicate the additional peaks (for the Set 2 sample) due to a distortion of the cubic perovskite structure. The numbers in parentheses (hkl values) correspond to tetragonal indexing and the ones without parentheses correspond to cubic indexing.
x = 0.6, in Set 2 and 3. For the x = 0.6 sample in Set 2 arrows indicate the additional peaks due to a tetragonal distortion. The small difference in structures in this case is perhaps due to different preparation conditions for Set 2 (arc melting), as compared to that of Set 3 (tantalum tube furnace method).

The orthorhombic perovskite structure has the GdFeO$_3$ structure [52], tetragonal and cubic structures being special cases of the GdFeO$_3$ structure. Figure 3.3 shows the GdFeO$_3$ structure. The tilting of the VO$_6$ octahedra results in a doubling of the c axis (relative to the cubic unit cell). For the case of LaVO$_3$, at room temperature, the x-ray diffraction peaks can be indexed based either on a GdFeO$_3$ unit cell (with a ~ b) or by doubling the cubic unit cell along the (cubic) a and b directions as well. Since $c/a\sqrt{2} \sim 1$, it is not possible to distinguish between the two cases.

In Figure 3.4 we plot the orthorhombic lattice parameters of LnVO$_3$ (from ref [30]) with the GdFeO$_3$ structure, where Ln is a rare earth element, as a function of the ionic radius of the rare earth element [55]. Lattice parameters a and c vary in a linear fashion with respect to the ionic radius, decreasing with decreasing size of the rare earth ion. Surprisingly though, the b lattice parameter does not show this simple behaviour. The cause for this (variation of b with ionic radius of the rare earth ion) is likely related to the tolerance factor. The tolerance factor, for the perovskite structure of general formula ABO$_3$, is defined as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$  \hspace{1cm} \text{(3.1)}$$

where $r_A$ is the ionic radius of the larger cation A etc. As we substitute rare earth elements with larger ionic radii the tolerance factor moves towards a value of 1 (see Figure 3.5). As the tolerance factor approaches 1, distortions are not necessary to stabilize the structure and hence the lattice parameters vary in a manner such that
Figure 3.3: The GdFeO$_3$ structure from ref. [52]
Figure 3.4: Lattice parameters, in Å, of LnVO₃ (where Ln is a rare earth atom), from ref. [30], as a function of the ionic radius of the rare earth atom.
Figure 3.5: Tolerance factor as a function of the ionic radius of the rare earth, in \( \text{LnVO}_3 \)
the crystal structure tends towards the undistorted cubic structure. In other words, the ratios $c/a\sqrt{2}$ and $c/b\sqrt{2}$ approach 1 with increasing value of the ionic radius of the rare earth ion, as shown in Figure 3.6. The predicted lattice parameters of LaVO$_3$ based on extrapolation of the available data for other LnVO$_3$ are in very good agreement with the experimentally determined lattice parameters for LaVO$_3$.

LaVO$_3$ has a cooperative Jahn-Teller distortion below the Néel temperature in order to lift the threefold orbital degeneracy of the ground state [53]. Dougier et al. [31] found that the room temperature structure was a tetragonal distortion of the cubic perovskite structure (GdFeO$_3$ structure with $a \sim b$) and as mentioned earlier the doubling of the unit cell in $a$ and $b$ directions as well would also lead to satisfactory indexing of the x-ray patterns. The structure changed at low temperatures (below $T_N$) to tetragonal (with $c/a < 1$, where $c$ and $a$ are doubled with respect to the cubic perovskite) [31]. Shirakawa et al. [73] found the low temperature structure to be of the orthorhombic perovskite (GdFeO$_3$) type, with $c/\sqrt{2}a < 1$. Dougier and Hagenmuller [31] reached a different conclusion probably because they carried out their study down to 77 K where the separation of the peaks due to the orthorhombic distortion may not be clear. Shirakawa et al. [73] conducted their study down to liquid helium temperatures. In our measurements (lowest temperature $\sim 27$ K) we did not find any change in the crystal symmetry below $T_N$. See Figure 3.7 where the peak position and profile of the 220 and 004 peak is seen to be unchanged with temperature. In order to get the lattice parameters, the peak positions were corrected using Si as an internal standard. The change in the lattice parameter of Si with temperature is neglected here since the change in its lattice parameter over a 300 K range is about 0.001 Å (see [54] for the thermal expansion coefficient), and the error
Figure 3.6: \( c/\sqrt{2} \) and \( c'/\sqrt{2} \) (where \( a, b, \) and \( c \) are the lattice parameters of \( LnVO_3 \) from ref. [30]) as a function of the ionic radius of the rare earth (\( Ln \)) atom.
Figure 3.7: Intensity $I$ versus the position $2\theta$ for the 220 (and 004) peak at different temperatures, for \( \text{LaVO}_3 \) (Set 2)
bars on our data are larger than that.

The lattice parameters are plotted as a function of temperature in Figure 3.8 for \( x = 0.9 \) and 1.0 (Set 2) and are seen to be roughly unchanged (±0.004 Å) with temperature.

TGA measurements were performed on the samples in order to determine their oxygen contents (see, for example, Figure 3.9). Assuming that the La and Sr contents of the samples are exactly as given by the nominal compositions, the oxygen contents were computed from the weight gained during the TGA scans, and are listed in Tables 3.1, 3.2, and 3.3. The precision of the data is ±0.0001 and the accuracy is ±0.001.

4-probe d.c. resistance measurements on one set of samples (Set 1) are shown in Figure 3.10, and Figure 3.11. The region \( x \leq 0.7 \) exhibits metallic behaviour whereas the low strontium concentration region is semiconducting, consistent with literature data [16, 17]. For the semiconducting samples, a linear variation of the logarithm of the resistance as a function of temperature enables us to determine the activation energy \( E_{\text{act}} \), as indicated in Figure 3.11. Resistivity measurements on single crystal LaVO₃ [33] yielded 0.16 eV for the activation energy.

**Magnetic Susceptibility Measurements**

**Theoretical review**

The total magnetic susceptibility of a non-magnetic metal is given by

\[
\chi = \chi_{\text{spin}} + \chi_{\text{orbit}}.
\]  

(3.2)

where

\[
\chi_{\text{spin}} = \chi_{\text{Pauli}}.
\]  

(3.3)
Figure 3.8: Lattice parameters a and c versus temperature T, for x = 0.9 and 1.0 (Set 2)
Figure 3.9: TGA scan, in pure oxygen, for $La_{0.9}Sr_{0.1}VO_3$ (Set 2)
Figure 3.10: The normalized resistance $R(T)/R(300 \, \text{K})$ as a function of temperature $T$ and $x$ for La$_x$Sr$_{1-x}$VO$_3$ (Set 1, metallic samples)
Figure 3.11: Logarithm of the resistance $\log_{10}(R)$ as a function of the inverse temperature $1/T$ for $x = 0.8, 1.0$ in $La_xSr_{1-x}VO_3$ (Set 1)
and

\[ \chi_{\text{orbit}} = \chi_{\text{Landau}} + \chi_{\text{core}} + \chi_{\text{VV}} \]  \quad (3.4)

Here, \( \chi_{\text{core}} \) is the diamagnetism due to the ion cores

\[ \chi_{\text{core}} = \frac{-N_A z e^2 \langle r^2 \rangle}{6mc^2}, \]  \quad (3.5)

where \( N_A \) is the Avogadro number, \( z \) is the number of nearest neighbours, \( e \) is the electronic charge, \( \langle r^2 \rangle \) is the mean square radius of the ion, \( m \) is the electronic mass, and \( c \) the speed of light. The paramagnetic Van Vleck (orbital) susceptibility for a metal is given by

\[ \chi_{\text{VV}} = \frac{2N_A \mu_B^2}{(2\pi)^3} \int \sum_{m' \neq m} \frac{f(\epsilon_{m'k}) - f(\epsilon_{mk})}{\epsilon_{m'k} - \epsilon_{mk}} |\langle m'k | L | mk \rangle|^2, \]  \quad (3.6)

where \( \epsilon_{m'k} \) is the energy of an electron in the band \( m \) with wave vector \( k \), \( f(\epsilon_{mk}) \) is the Fermi function, \( L \) is the orbital angular momentum operator, \( \mu_B \) is the Bohr magneton and the integral is over the Fermi surface. \( \chi_{\text{Pauli}} \) is the conduction electron spin susceptibility which, in the free electron approximation, is

\[ \chi_{\text{Pauli}}^{\text{free electron}} = N_A \mu_B^2 D(\epsilon_f) \]  
\[ = N_A \mu_B^2 \frac{V_{\text{cell}}}{2\pi^2} \frac{2m}{\hbar^2} \frac{3}{2} \epsilon_f \frac{1}{2}, \]  \quad (3.7)

where \( D(\epsilon_f) \) is the density of states at the Fermi level \( (\epsilon_f) \), \( V_{\text{cell}} \) is the volume of a unit cell, and \( \hbar \) is the Planck's constant divided by \( 2\pi \). The Landau contribution for free electrons is

\[ \chi_{\text{Landau}}^{\text{free electron}} = -\frac{1}{3} \chi_{\text{Pauli}} \]  \quad (3.8)
If band structure effects may be represented by an effective mass $m^*$ and enhancements due to exchange and correlation effects are taken into account the Pauli susceptibility takes the form

$$\chi_{\text{Pauli}} = \frac{(m^*/m)}{1 - \alpha} \chi_{\text{Pauli}} \text{ free electron},$$

(3.9)

where $1/(1-\alpha)$ is the Stoner enhancement factor. The general form of this is the same in the Fermi liquid approach, the Stoner model, and the Hubbard model [56]. The Landau susceptibility is modified as follows

$$\chi_{\text{Landau}} = -\frac{1}{3} \left( \frac{m}{m^*} \right)^2 \chi_{\text{Pauli}}(1 - \alpha)$$

(3.10)

Results and discussion

La$_x$Sr$_{1-x}$VO$_3$ ($0.1 \leq x \leq 0.9$) The magnetization versus applied field $(M(n))$ isotherms are shown in Figure 3.12 through Figure 3.15 for samples in Set 3. From these isotherms, the contribution due to ferromagnetic impurities was obtained and subtracted from the susceptibility data.

The variations of the measured molar susceptibility with temperature for the La$_x$Sr$_{1-x}$VO$_3$ samples (Set 3) is shown in Figure 3.16. Low temperature Curie terms, presumably arising from isolated magnetic defects are apparently present. They have been subtracted and the resulting corrected data, $\chi^\text{corr}(T)$, are plotted in Figure 3.17. In case there are isolated magnetic defects in the material under investigation, we get an additional term in the susceptibility of the form $C_M/T$ where

$$C_M = \frac{nN_Ag^2\mu_B^2S(S+1)}{3k_B}$$

(3.11)
Figure 3.12: Magnetization versus applied field $M(H)$ isotherms for La$_{0.1}$Sr$_{0.9}$VO$_3$ (Set 3)
Figure 3.13: Magnetization versus applied field $M(H)$ isotherms for $\text{La}_{0.3}\text{Sr}_{0.7}\text{VO}_3$ (Set 3)
Figure 3.14: Magnetization versus applied field $M(H)$ isotherms for La$_{0.5}$Sr$_{0.5}$VO$_3$ (Set 3)
Figure 3.15: Magnetization versus applied field $M(H)$ isotherms for $La_{0.7}Sr_{0.3}VO_3$ (Set 3)
Figure 3.16: The molar susceptibility without any correction for a Curie term $\chi_M$ as a function of temperature $T$ and $x$ for La$_x$Sr$_{1-x}$VO$_3$ samples in Set 3
Figure 3.17: The corrected molar susceptibility $\chi_M^{\text{corr}}$ as a function of temperature $T$ and $x$ for La$_x$Sr$_{1-x}$VO$_3$ samples in Set 3
where \( n \) pertains to the number of moles of \( S = 1/2 \) isolated magnetic defects per mole of \( \text{La}_x\text{Sr}_{1-x}\text{VO}_3 \) (in our case). Assuming the form of the susceptibility to be

\[
\chi = \chi_0 + \frac{C_M}{T},
\]

we can extract the Curie term by plotting \( \chi T \) versus \( T \) and then extrapolating the data to zero temperature to get \( C_M \) (this is possible when \( \chi_0 \) is only weakly temperature dependent). As seen in Figure 3.18 \( \chi T \) versus \( T \) is linear for our data in the low temperature (< 100 K) region. For our samples \( n \), (concentration of \( S = 1/2 \) isolated magnetic defects) varies between 0.2 to 0.5% per mole of \( \text{La}_x\text{Sr}_{1-x}\text{VO}_3 \).

\( \chi^\text{opt}_M (300 \text{ K}) \) appears to be smoothly varying with \( x \) (see Figure 3.19) across the complete \( x \) range. Using equations 3.7, 3.9, and the following equation

\[
\epsilon_f = \frac{\hbar^2}{2m}(3\pi^2n)^{2/3},
\]

where \( n \) is the electron concentration, we get

\[
\chi(x) = 0.194\left(\frac{m^*}{m}\right)(1 - x)^{1/3},
\]

where we have not considered the corrections due to \( \chi_{\text{core}} \) and \( \chi_{\text{VV}} \) (which are opposite in sign) and we have included all the enhancement effects in the effective mass ratio. In equation 3.14 the susceptibility is in units of \( 10^{-4} \text{ cm}^3/\text{mole} \), \( x \) is the lanthanum content and 0.194 is the free electron Pauli spin susceptibility (in units of \( 10^{-4} \text{ cm}^3/\text{mole} \), for a carrier concentration of 1 electron per unit cell).

Calculation based on the above assumptions gives the following effective mass ratio for two metallic samples. For \( x = 0.1 \) and 0.7, \( m^*/m = 11 \) and 41 respectively. These are very high values compared to those of normal metals and these high values are reminiscent of heavy fermion materials. A more refined analysis of the problem at
Figure 3.18: Product of the molar susceptibility $\chi_M$ and the temperature $T$ as a function of $T$ for $\text{La}_{0.1}\text{Sr}_{0.9}\text{VO}_3$ (Set 3)
Figure 3.19: The corrected molar susceptibility at 300 K $\chi_M^{corr}(300 \text{ K})$ as a function of the lanthanum doping level $x$ for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ (Set 3)
hand will have to await the analysis of Chapter 4 where we show that \(\lambda_{VV}\) plays a significant role and that band structure enhancements and exchange and correlation based enhancements (to the susceptibility) need to be treated separately.

For the case of La\(_{0.9}\)Sr\(_{0.1}\)VO\(_3\), the magnetic susceptibility exhibits two anomalies (see Figure 3.20). The high temperature anomaly at \(T_N = 110\) K presumably corresponds to antiferromagnetic ordering. The second anomaly (below \(T_N\)) occurs at different temperatures depending on whether the sample is field-cooled (FC) or zero-field-cooled (ZFC). In the FC case the second anomaly is at 100 K and at 15 K in the ZFC case. For the \(x = 0.9\) sample we expect that a fraction of vanadium ions will be in the \(\text{V}^{3+}\) oxidation state. Therefore, the mechanism of double exchange is likely to play a part. Double exchange was first proposed by Zener in 1951 [57] in order to explain the magnetic and transport properties of La\(_x\)Sr\(_{1-x}\)MnO\(_3\). In our case the double exchange refers to the coupling between \(\text{V}^{3+}\) and \(\text{V}^{4+}\) ions via the intervening \(\text{O}^{2-}\) ion. This tends to align the spins on the vanadium ions in a ferromagnetic fashion. This competes with the antiferromagnetic superexchange between \(\text{V}^{3+}\) ions. The implications of such a situation were discussed in detail by de Gennes [58]. Clearly, in view of the competing ferromagnetic and antiferromagnetic couplings the equilibrium configuration of such a system might be canted. de Gennes predicted the existence of a second anomaly below \(T_N\) at which point the susceptibility diverges. Below this temperature the spin configuration is canted. Such behavior has been observed in antiferromagnetic CrSb doped with a small amount of MnSb [59]. We see similar behaviour (Figure 3.20) except for the fact that in the FC experiment the susceptibility anomaly (below \(T_N\)) occurs at a higher temperature compared to the ZFC case. This is perhaps because the presence of a field while cooling provides
Figure 3.20: Zero-field-cooled (ZFC) and field-cooled (FC) susceptibility as a function of temperature for La$_{0.9}$Sr$_{0.1}$VO$_3$ (Set 3). The cooling field and the measuring field is 10 kGauss.
a preferred direction for the spins to align and a direction for the canted moment.

From the $\chi(T)$ data for the three set of samples prepared we find that the samples with a vanadium valence less than +3.2 order antiferromagnetically with a Néel temperature $T_N$ which is a function of the effective vanadium oxidation state as shown in Figure 3.21. We calculate the effective vanadium oxidation state ($v$) based on the oxygen content as determined from the TGA measurements. As can be seen from Tables 3.1, 3.2, and 3.3, the Néel temperature is sensitive to both the strontium concentration and the oxygen content, as reflected in $T_N(v)$.

The case of LaVO$_3$ Magnetic susceptibility of LaVO$_3$ (Figure 3.22, Set 3) exhibits a peak at 145 K, indicative of antiferromagnetic ordering. The data for the sample from Set 2 are shown in Figure 3.23. The data below $T_N$ are seen to be significantly different for the two samples. This may be related to the differing oxygen contents of the two samples. Table 3.4 lists the value of the Néel temperature $T_N$, the paramagnetic Curie temperature $\theta$, and the effective moment per vanadium $\mu_{\text{eff}}$ for LaVO$_3$ as obtained by other workers. The considerable disagreement among various results is thought to be due to differing oxygen contents in the various samples.

Moreover, the values obtained for $\theta$ and $\mu_{\text{eff}}$ are rather sensitive to the presence of any temperature independent terms (diamagnetism of the ion cores $\chi_{\text{core}}$ and the Van Vleck susceptibility $\chi_{\text{VV}}$, for instance) in the susceptibility. As an example, a Curie-Weiss fit to the raw data, between 350 K and 400 K, yields $\theta = -581$ K and $\mu_{\text{eff}} = 3.33 \mu_B$. On the other hand, if we correct the data for $\chi_{\text{core}} (= -0.66 \times 10^{-1} \text{ cm}^3/\text{mole} \ [67])$ and assume, for the purpose of demonstration, that $\chi_{\text{VV}} = 2.1 \times 10^{-4} \text{ cm}^3/\text{mole}$ (same as in V$_2$O$_3$ which has trivalent vanadium [72]), then a Curie-
Figure 3.21: Variation of the Néel temperature $T_N$ with the vanadium valence $v$, for the three sets of $La_xSr_{1-x}VO_3$ samples.
Figure 3.22: The molar susceptibility $\chi_M$ as a function of temperature $T$ for LaVO$_3$ (Set 3). The susceptibility is measured in a field of 10 kGauss on warming, in field-cooled (FC) as well as zero-field-cooled (ZFC) cases.
Figure 3.23: The molar susceptibility $\chi_M$ as a function of temperature $T$ for LaVO$_3$ (Set 2). The susceptibility is measured in a field of 10 kGauss on warming, in field-cooled (FC) as well as zero-field-cooled (ZFC) cases.
Table 3.4: Values of the Neel temperature $T_N$, the paramagnetic Curie temperature $\theta$ and the effective moment per vanadium $\mu_{\text{eff}}$ for LaVO$_3$ as obtained by other workers

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_N$ (K)</th>
<th>$\theta$ (K)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>144</td>
<td>-665</td>
<td>3.84</td>
</tr>
<tr>
<td>6</td>
<td>156</td>
<td>-400</td>
<td>3.07</td>
</tr>
<tr>
<td>7</td>
<td>135</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>&lt; 150</td>
<td>-400</td>
<td>2.83</td>
</tr>
<tr>
<td>9</td>
<td>137</td>
<td>Does not obey C-W law</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>128</td>
<td>-1000</td>
<td>4.2</td>
</tr>
<tr>
<td>This work (Set 1 and 2)</td>
<td>140</td>
<td>see text</td>
<td>see text</td>
</tr>
<tr>
<td>This work (Set 3)</td>
<td>145</td>
<td>see text</td>
<td>see text</td>
</tr>
</tbody>
</table>
Weiss fit, between 350 K and 400 K, to the corrected data yields $\theta = -487$ K and $\mu_{\text{eff}} = 3.0 \mu_B$ which is closer to the expected value of $2.83 \mu_B$ for $S = 1$ and $g = 2$. Hence, in light of the uncertainty in determining the temperature independent terms in the susceptibility, the values obtained for $\theta$ and $\mu_{\text{eff}}$ may perhaps not be very meaningful. Our value of $T_N$ is close to that obtained by Zubkov et al. [29] from neutron diffraction.

The susceptibility below $T_N$ depends on the cooling conditions (i.e. whether the sample is cooled in a field or not). In particular, note that the susceptibility is higher in the case of a zero-field-cooled (ZFC) measurement as compared to that of a field-cooled (FC) measurement and there is a second anomaly (at $T \sim 140$ K) below $T_N$, see Figure 3.22, as in the case of $x = 0.9$ (here for the Set 3 sample, the anomaly occurs at the same temperature for ZFC as well FC cases). Also, the compound LaVO$_3$ exhibits hysteresis in magnetic moment vs. applied field $(M(H))$ isotherms (for ZFC as well as FC cases, see Figure 3.24 and Figure 3.25). Also, shown in Figure 3.26 through Figure 3.30 are ZFC isotherms at different temperatures for the LaVO$_3$ sample in Set 2. The remanent ferromagnetic moment as deduced from $M(H)$ isotherms is found to go to zero at $T_N$ (Figure 3.31; the data are for the LaVO$_3$ samples from Set 2 and 3 which had $T_N$'s of 140 K and 145 K, respectively). This is consistent with a ferromagnetic component to the spin ordering due to canting of spins and/or due to ferrimagnetism, as will be discussed later. The ferromagnetic moment is small amounting to only $(1.7$ to $3.3) \times 10^{-3} \mu_B/V$ at lowest temperatures. LaVO$_3$ is known to have a structural phase transition, from tetragonal to orthorhombic, near $T_N$ [31, 33, 34]. As mentioned earlier we did not observe this transition. But, even in a tetragonal structure the point symmetry of the vanadium atoms lacks inversion
Figure 3.24: Magnetization versus field $M(H)$ hysteresis curve for LaVO$_3$ (Set 3), for a zero-field-cooled (ZFC) experiment, at 5K. The remanent moment $M_R$ is indicated.
Figure 3.25: Magnetization versus field $M(H)$ hysteresis curve for LaVO$_3$ (Set 3), for a field-cooled (FC) experiment, at 5K
Figure 3.26: Magnetization versus field $M(H)$ hysteresis curve for LaVO$_3$ (Set 2), for a zero-field-cooled (ZFC) experiment, at 10K
Figure 3.27: Magnetization versus field $M(H)$ hysteresis curve for LaVO$_3$ (Set 2), for a zero-field-cooled (ZFC) experiment, at 50K
Figure 3.28: Magnetization versus field $M(H)$ hysteresis curve for LaVO$_3$ (Set 2), for a zero-field-cooled (ZFC) experiment, at 100K
Figure 3.29: Magnetization versus field $M(H)$ hysteresis curve for $\text{LaVO}_3$ (Set 2), for a zero-field-cooled (ZFC) experiment, at 125K.
Figure 3.30: Magnetization versus field M(H) hysteresis curve for LaVO$_3$ (Set 2), for a zero-field-cooled (ZFC) experiment, at 135K
Figure 3.31: The remanent magnetization $M_R$ as a function of temperature $T$ for LaVO$_3$ (Set 2 and Set 3), as obtained from M(H) isotherms at different temperatures. The solid line is drawn as a guide to the eye.
symmetry. This gives rise to a non-zero Dzyaloshinsky-Moriya [62, 63] interaction responsible for the canting of spins. The susceptibility for a system exhibiting canting has been theoretically derived by Moriya [63]. In the vicinity of the Néel temperature, the susceptibility perpendicular to the easy axis (of magnetization) deviates from the Curie-Weiss law and, in the mean field approximation, is given by

\[ \chi_\perp = \frac{N_A \mu_{\text{eff}}^2}{3k_B(T + T_N)} \left( \frac{T - T_0}{T - T_N} \right) \]

where \( N_A \) is the Avogadro number, \( \mu_{\text{eff}} \) is the effective moment and \( k_B \) the Bohr magneton. \( T_N \) is the Néel temperature and is expressed as follows

\[ T_N = \frac{JzS(S + 1)}{3k_B} \left[ 1 + \left( \frac{D}{J} \right)^2 \right]^{1/2} \]

\[ T_0 = \frac{JzS(S + 1)}{3k_B} \quad (3.16) \]

\[ T_0 = \frac{JzS(S + 1)}{3k_B} \quad (3.17) \]

where \( J \) is the exchange coupling constant \( (H_{ij} = J S_i S_j) \), \( z \) is the number of nearest neighbours. \( S \) is the spin and \( D \) is the Dzyaloshinski-Moriya interaction coupling constant. The susceptibility parallel to the easy axis of magnetization \( \parallel \) is still given by the Curie-Weiss law. For a polycrystalline sample, the total susceptibility is given by

\[ \chi = \frac{2}{3} \chi_\perp + \frac{1}{3} \chi_\parallel \quad (3.18) \]

Clearly, \( T_0 < T_N \) from equation 3.17 so we would expect (from equation 3.15) that near \( T_N \) the susceptibility will show a positive deviation from a Curie-Weiss law. However, in fact, we observe a negative deviation from the Curie-Weiss behaviour, near the Néel temperature (see Figure 3.32). Here, we have made use of a Curie-Weiss fit between 350 K and 400 K, to the susceptibility data corrected for \( \chi_{\text{core}} = \)
Figure 3.32: The molar susceptibility of LaVO₃ (Set 3), corrected for $\chi_{\text{core}}$ and $\chi_{\text{VV}}$ (see text), as a function of temperature. Also shown is a Curie-Weiss fit to the data between 350 K and 400 K.
-0.66 \times 10^{-4} \text{ cm}^3/\text{mole and } \chi_{YY} = 2.1 \times 10^{-4} \text{ cm}^3/\text{mole}, in order to get a value for the asymptotic Curie temperature and the effective moment.

A second mechanism which could give rise to canting is double exchange, discussed earlier. The presence of V^{4+} in LaVO_{3} perhaps occurs because our samples are slightly off stoichiometry. However, in this case the sign of the anomaly is opposite to that predicted (i.e. susceptibility exhibits a dip towards zero (or -\infty) instead of diverging below T_{N} as predicted). This is perhaps related to the diamagnetism observed in this compound.

It is seen from the FC isotherm (Figure 3.25) that in low fields the sample exhibits a diamagnetic moment. The slope of the isotherms is, however, paramagnetic (positive) in the complete field range (see Figure 3.33 and Figure 3.34). In fact, the susceptibility (\chi = M/H), below T_{N} and in low fields, is found to be negative (see Figure 3.35). This is obviously due to the fact that we have taken the susceptibility to be M/H and this is certainly not appropriate (especially in low fields) when the isotherm is shifted from the origin. The diamagnetism observed in this compound is quite similar to that seen in ferrimagnetic spinels, such as Co_{2}VO_{4} [60] and Co_{2}TiO_{4} [61], where there are two sublattices (antiferromagnetically aligned) with ions in crystallographically inequivalent positions and a spontaneous magnetization results from the incomplete cancellation of the magnetic moments of the two sublattices. The spontaneous magnetization is a sum of the magnetizations of each sublattice and a sign reversal of the net magnetization could occur due to different temperature dependences of the individual sublattice magnetizations. In the case of LaVO_{3}, some of the vanadium ions may be magnetically inequivalent perhaps due to clustering of V^{4+} ions and/or due to the presence of (slightly) crystallographically inequivalent
Figure 3.33: Magnetization versus field $M(H)$ hysteresis curves for LaVO$_3$ (Set 2), under different cooling fields, at 5K.
Figure 3.34: Magnetization versus field $M(H)$ hysteresis curves for $\text{LaVO}_3$ (Set 3), under different cooling fields, at 5K
Figure 3.35: The molar susceptibility of LaVO₃ (Set 3) as a function of temperature, when the sample was field-cooled (FC) in the fields indicated in the figure. The measuring field is the same as the cooling field for the FC experiments. For the zero-field-cooled (ZFC) curve, the measuring field is 1000 G.
sites for the vanadium (which might give rise to different extents of quenching of the orbital magnetic moment and make them magnetically inequivalent) and this might give rise to the diamagnetism observed. As is seen in Figure 3.34, if the sample is cooled in 10 kGauss then the remanent magnetic moment in zero field is positive (although, if the sample is cooled in lower fields the remanent moment in zero field is negative). This is because a field of 10 kGauss is presumably able to overcome the anisotropy and hence rotate the weak ferromagnetic moment in the direction of the applied field. The corresponding field required to rotate the moments is somewhat higher for the Set 2 sample (see Figure 3.33). On the other hand the remanent moment for a ZFC sample is zero because the different (weakly) ferromagnetic domains are oriented so as to give a zero net magnetic moment (to minimize energy).

We performed resistivity measurements on LaVO₃ under various conditions of cooling and applied field (Figure 3.36). It is seen that unlike the susceptibility, the resistivity is rather immune to whether the sample is zero-field-cooled or not. We do not see any transition to zero resistance at the temperature at which the susceptibility becomes diamagnetic.

The x = 0.9 sample (from Set 3) did show a different susceptibility below the Néel temperature depending on the cooling conditions (see Figure 3.20). However, in this case the field-cooled sample had a higher susceptibility below the Néel temperature than the zero-field-cooled one. Also, this was a much smaller effect as compared to the difference seen for LaVO₃.
Figure 3.36: Logarithm of the resistance \( \log(R) \), for \( \text{LaVO}_3 \) (Set 2), as a function of \( 1000/T \), where \( T \) is the temperature, under the following conditions; zero-field-cooled and measured in zero applied field \( \text{ZFC}(H=0) \), zero-field-cooled and measured in an applied field of 10 kGauss \( \text{ZFC}(H=10 \text{ kGauss}) \), field-cooled in 1 Tesla and measured in zero applied field \( \text{FC}(H=0) \), and field-cooled and measured in an applied field of 10 kGauss \( \text{FC}(H=10 \text{ kGauss}) \).
Theoretical review

Consider a nucleus of spin \( I \), 2\( I + 1 \) fold degenerate. This degeneracy can be lifted by the application of a magnetic field \( H_0 \) due to the Zeeman effect, which has the following interaction term in the Hamiltonian

\[ H = -\mu_n \cdot H_0 \]  

(3.19)

where \( \mu_n \) is the nuclear magnetic moment (\( = \gamma_n h I \), with \( \gamma_n \) the nuclear gyromagnetic ratio, and \( h \) is the Planck's constant divided by \( 2\pi \)). As a result one gets equally spaced levels of separation \( \gamma_n h H_0 \) (see Figure 3.37). If in addition to the dc field, we apply an rf field perpendicular to \( H_0 \) such that \( \hbar \omega_0 = \hbar \gamma_n H_0 \), where \( \omega_0 \) is the frequency of the rf field, then there will be a resonant absorption of energy by the spin system due to transitions between adjacent levels and this is referred to as nuclear magnetic resonance (NMR).

The term in the Hamiltonian which describes the coupling mechanism, between electronic and nuclear spins, in a metal is

\[ H = -\frac{8\pi}{3} \mu_e \cdot \mu_n \delta(r) \]  

(3.20)

where \( \mu_e = -\gamma_e h S \) and \( \mu_n = \gamma_n h I \). Here, \( \gamma_e \) is the gyromagnetic ratio of the electron. The static part of this interaction (involving \( I_S S_z \)) gives rise to an effective hyperfine field at the site of the nucleus given by

\[ \Delta H = \frac{8\pi}{3} \frac{\langle |u_k(0)|^2 \rangle}{E_S} H_0 \]  

(3.21)

where \( H_0 \) is the applied field, \( \chi \) is the spin susceptibility of the conduction electrons, \( u_k(0) \) is the electronic wave function at the position of the nucleus and the average
Figure 3.37: Energy level diagram for nucleus of spin I in an applied field of $H_0$ demonstrating the nuclear Zeeman effect.
is over the Fermi surface (FS). This gives rise to a shift in the resonance frequency, \( \omega_0 = \gamma n \Pi_0 (1 + \kappa) \), where \( \kappa \) is called the Knight shift and is given by

\[
\kappa = \frac{8\pi}{3} < |u_k(0)|^2 >_{FS} \quad (3.22)
\]

The Knight shift is generally independent of temperature, of frequency (or field), and increases with increasing atomic number.

Once the nuclei have been excited from the ground state by the rf field, they will attain equilibrium and get back to the ground state by the process of relaxation. Phenomenologically, this is accomplished by spin-spin and spin-lattice relaxation. In the former case, equilibrium is established in the nuclear spin system by spin-spin interactions. Spin-lattice relaxation causes transitions of the nuclei to the ground state by exchange of energy between the nuclear spins and the lattice (electrons).

The tranverse part of the Hamiltonian of eqn. 3.20 contains the terms \( I_x S_x + I_y S_y \) (= \( 1/2(I_+ S_- + I_- S_+) \)), where \( I_\pm \) and \( S_\pm \) are the usual raising and lowering operators. These can induce transitions between adjacent nuclear Zeeman levels and bring about spin-lattice relaxation. The spin-lattice relaxation time \( (T_1) \) is given by

\[
\kappa^2 T_1 = \frac{\hbar}{4\pi k_B T} \left( \frac{\gamma e}{\gamma_n} \right)^2 \quad (3.23)
\]

This is known as the Korringa relation [64].

The line width in the case of NMR arises from homogeneous and inhomogeneous broadening mechanisms. Homogeneous broadening is due to a coupling between the nuclear spins. The nuclear dipole-dipole interaction produces a magnetic field at the site of each nucleus thereby modifying the local field and giving rise to a line width due to different resonance frequencies of the various nuclei. Inhomogeneous broadening, on the other hand, is due to factors such as inhomogeneity of the applied
magnetic field, demagnetization effects due to the shape of the sample, due to a large susceptibility of the electrons giving rise to variations in the local field, and quadrupolar interactions. Inhomogeneous broadening is generally field dependent.

For the case of transition metals, in which it is the d-electrons which primarily determine the magnetic properties of the material, there are three principal contributions to the Knight shift (and in a similar manner the relaxation rate also). The first contribution is called the Fermi contact interaction which is due to unpaired s electrons in the system and is the one in eqn. 3.22. The d electrons have a wave function which is zero at the site of the nucleus and so a zero hyperfine coupling constant. However, the d electrons can polarize the inner s electrons and indirectly give rise to an effective field at the site of the nucleus. This is known as core polarization. An additional term is due to the (orbital) Van Vleck susceptibility of the d electrons which gives rise to a shift in the resonance frequency.

Measurements of the Knight shift, of the line width and of the spin–lattice relaxation rate were performed for the $^{51}$V nucleus on the second set of La$_x$Sr$_{1-x}$VO$_3$ samples, referred to as Set 2 in this paper (see Table 3.2). Measurements were made on some of the samples in Set 3 as well and they were found to be in agreement with our data on Set 2.

**Discussion of results, $x \neq 1$**

**Knight shift**  The Knight shift $\kappa$ is defined as $(\nu - \nu_{\text{ref}})/\nu_{\text{ref}}$ where $\nu$ is the resonance frequency of the given sample and $\nu_{\text{ref}}$ is the resonance frequency of the reference sample (the resonance frequency for NaVO$_3$ in this case, see [70]) in a fixed magnetic field. The variation of the Knight shift $\kappa$ at room temperature
versus the La doping level $x$ in $La_xSr_{1-x}VO_3$ is shown in Figure 3.38. Between $x = 0.1$ and $x = 0.7$ in the metallic phase, $\mathcal{K}$ is nearly independent of $x$. Upon traversing the metal-insulator transition near $x = 0.8$, $\mathcal{K}$ decreases strongly from $\mathcal{K} = +0.14\%$ ($x = 0.7$) to $\mathcal{K} = -0.55\%$ ($x = 0.9$) and then is constant to $x = 1.0$. In the metallic phase, for $x \leq 0.7$, the Knight shift is temperature independent as shown in Figure 3.39. For the samples with $x \geq 0.7$, the measurements of the Knight shift are affected by a larger error due to the inhomogeneous broadening of the NMR line (see Figure 3.40). For $x = 0.8, 0.9$ and 1.0 the data refer to the CW measurements in low field (10 kGauss). It should be noted that for $x = 0.7$, the inhomogeneous magnetic broadening appears to be asymmetric. As shown in Figure 3.40, a shoulder on the low frequency side is present corresponding to a small negative Knight shift value. Furthermore, in $LaVO_3$ and the other semiconducting samples with $x = 0.8$ and 0.9, a signal with a small negative shift was observed at low temperatures. This small signal could be observed only with the pulsed method in a field of 82 kGauss and it becomes narrower with decreasing temperature with a shift which is weakly temperature dependent and approaches zero at low temperatures (see Figure 3.39). It is conceivable that this signal (with a small negative Knight shift which is only weakly temperature dependent) originates from the presence, in the samples, of a minority phase containing non-magnetic vanadium atoms.

**Line width and relaxation rate** The $^{51}V$ NMR line width $\Delta$ was determined as discussed in Chapter 2. and was found to be both $x$ and $H$-dependent. The NMR spectra in the 82 kGauss magnet for some of the samples are shown in Figure 3.40, the $H$-dependence indicates that in all cases a field-dependent inhomogeneous broadening
Figure 3.38: Variation of the Knight shift $\mathcal{K}$ as a function of the La doping level $x$ in La$_x$Sr$_{1-x}$VO$_3$
Figure 3.39: Variation of $\mathcal{K}$ with temperature $T$ for metallic $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ samples with $x \leq 0.7$ and of $\mathcal{K}(T)$ for the signal observed in 82 kGauss in the paramagnetic samples with $x \geq 0.8$. Also shown is the room temperature value of $\mathcal{K}$ for $x = 1.0$ with the CW method in 10 kGauss.
Figure 3.40: Three typical examples of NMR spectra taken at room temperature and in 82 kGauss for $\text{La}_{x}\text{Sr}_{1-x}\text{VO}_3$ samples with different lanthanum concentration $x$. The line for $x = 0.2$ is obtained from the Fourier transform (FT) of the free precession after a $\pi/2$ pulse. The spectrum for $x = 0.5$ is the FT of half of the echo after a $\pi/2-\pi$ pulse sequence. The spectrum for $x = 0.7$ is the plot of the frequency swept echo amplitude.
mechanism of magnetic origin is present. The field dependences of $\Delta$ at 300 K for the samples are shown in Figure 3.41. We anticipate that $\Delta(H)$ for each sample follows a linear relationship:

$$\Delta(x, H) = \Delta_0(x) + A_0(x)H$$  \hspace{1cm} (3.24)

At room temperature we took data near 10 kGauss with the CW method and at 82 kGauss with the pulsed FT of half of the echo and with the frequency swept echo height method (see Chapter 2). The values of $\Delta_0$ and $A_0$ were obtained by fitting a straight line to the available data for each sample, as shown in Figure 3.41. For $x \geq 0.8$, only one data point for the line width, near 10 kGauss, is available (the signal in 82 kGauss is very broad and since the spin-spin relaxation time $T_2$ is also very short, the frequency swept echo amplitude method could not be used to map the NMR line). Assuming that the homogeneous width for $x \geq 0.8$ is at least equal to the (homogeneous) width for $x = 0.7$, we get an estimate for the lower bound on $\Delta_0$. The estimated values of $\Delta_0$ and $A_0$ are affected by a large uncertainty ($\pm 10^{-15}$ kHz). The results are shown in Figure 3.42 and Figure 3.43. The abrupt increase of $A_0$ at the metal-insulator transition indicates the formation of localized moments in the insulating phase whereas the large homogeneous broadening in this phase is associated with the interaction of the $^{51}$V nuclei with nearby localized moments. The variation of the homogeneous width $\Delta_0$ with $x$ is also indicative of a paramagnetic insulator for $x > 0.7$ and of a metallic phase without local moments for $x < 0.7$. In
Figure 3.41: Variation of the line width $\Delta$ with the magnetic field $H$ for different $x$ in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$. 
Figure 3.42: The homogeneous linewidth $\Delta_0$ at room temperature versus $x$ for $La_xSr_{1-x}VO_3$
Figure 3.43: Inhomogeneous field dependent broadening parameter $A_0$ versus $x$ for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$, where the linewidth (Figure 2.27) follows $\Delta(x, H) = \Delta_0(x) + A_0(x)H$
fact, the value of 10 kHz for $A_{\Omega}$ in the metallic phase ($x < 0.7$, see Figure 3.42) is of the order of magnitude of the line width expected from nuclear dipole-dipole interactions. On the other hand, the larger $A_{\Omega}$ observed for $x > 0.7$ (see Figure 3.42) is due to a lifetime broadening of the $^{51}$V NMR line. The line width of a nucleus interacting with a localized moment can be written as [66]

$$\delta \omega = \gamma^2 \sqrt{2\pi/3(A/\hbar)^2} S(S+1)/3\omega_e,$$  (3.25)

where the hyperfine coupling constant $A/\hbar$ is in Gauss, $\gamma$ is the gyromagnetic ratio in rad/sec-G and the electronic exchange frequency $\omega_e$ is given by

$$\omega_e^2 = 2J^2zS(S+1)/3\hbar^2,$$  (3.26)

where $z = 6$ is the number of nearest neighbours of a given $V^{3+}$ localized moment and the exchange interaction constant $J = 3k_B T_N/2S(S+1)z$. For $T_N = 140$ K and spin $S = 1$, we get $\omega_e = 6.5 \times 10^{12}$ rad/sec. For a hyperfine field due to core polarization by d-electrons $H_{hf,d} = A/\hbar = -125$ kG/µB [70] one finds $A_{\Omega} = \delta \omega/2\pi = 73$ kHz in reasonable agreement with the experimental value for $x > 0.7$ (~ 60 kHz, see Figure 3.42). The behaviour of the parameters for the sample with $x = 0.7$ is to be noted. While the Knight shift value is the one pertaining to the metallic phase ($x < 0.7$), both the inhomogeneous and the homogeneous broadening are already evidencing the presence of randomly distributed localized moments in the metallic matrix. Furthermore, a small inhomogeneous magnetic broadening is present in the metallic phase also ($x < 0.7$). Since the broadening increases with the La content (see Figure 3.43), it is unlikely that this is due to paramagnetic impurities. It is conceivable that local spin density oscillations are present in the metallic phase due to the random distribution of Sr$^{2+}$ and La$^{3+}$ ions in the lattice.
The case of LaVO₃

The $^{51}$V NMR signal (as seen by the CW spectrometer) for LaVO₃ is very broad even at room temperature (Figure 3.44). The resonance line-width shows critical broadening (Figure 3.45) as one approaches the antiferromagnetic ordering temperature, typical of paramagnets (insulators). The signal disappears below $T_N$ since the internal field shifts the resonance beyond the region of experiment. The disappearance of the signal is generally considered a sign of magnetic ordering. The $^{51}$V Knight shift (paramagnetic shift) is $-0.55\%$. We were unable to see this signal at room temperature by the pulse method. This would appear to be due to a very short $T_2$ (spin-spin relaxation time) due to strong fluctuating local moments bringing about rapid de-excitation of the nuclei from the excited state to the ground state. However, we have observed a signal with a shift of $\approx + 0.07\%$ in a field of 58.92 kGauss by the pulse method (Figure 3.46). The signal persists below $T_N$ and the frequency shift and the resonance line-width (as obtained by plotting the amplitude of the spin-echo as a function of frequency) are independent of temperature. It is possible that the signal comes from some impurities in the sample although the sample was found to be x-ray pure. The other possibility is that $V^{4+}$ holes give rise to this signal. These holes would then appear to be mobile and relatively unaffected by the strong internal field which is present below $T_N$. The magnetic field at a $V^{4+}$ site would be small (a few kGauss) due to the cancellation of the internal field of the neighbouring spins.

The evolution of the spin-lattice ($T_1^{-1}$) and the spin-spin ($T_2^{-1}$) relaxation rates at room temperature as a function of composition $x$, shown in Figure 3.47 and Figure 3.48, gives a further confirmation that the transition from the metallic to the
Figure 3.44: $^{51}$V NMR lineshape obtained for LaVO$_3$ (Set 2) in a CW experiment at room temperature with a modulating field (peak-to-peak) of 16 Gauss.
Figure 3.45: $^{51}$V NMR linewidth $\Delta$ as a function of the temperature $T$ for $\text{LaVO}_3$ (Set 2). The solid line is drawn as a guide to the eye.
Figure 3.46: Amplitude of the spin-echo as a function of the frequency in a field of 58.92 kGauss, for LaVO₃ (Set 3), at two different temperatures. The solid line is drawn as a guide to the eye.
Figure 3.47: The variation of the spin-lattice ($T_1^{-1}$) relaxation rate at room temperature as a function of $x$ in $La_xSr_{1-x}VO_3$. 
Figure 3.48: The variation of the spin-spin relaxation rate $T_2^{-1}$ as a function of $x$ in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$
insulating phase is accompanied by the localization of the magnetic moment on the V site. For the paramagnetic insulating phase \((x > 0.7)\), the values of \(T_1^{-1}\) are estimated from the homogeneous line width since the pulse method can only yield an upper limit of \(T_1 \leq 10\mu s\). This result is consistent with the condition \(T_1 = T_2\) typical of lifetime broadening of the NMR line as observed in many paramagnetic insulators \[65\]. The temperature dependence of \(T_1^{-1}\) for \(x \leq 0.6\) is shown in Figure 3.49. The Korringa-like behaviour with \(T_1 T = 0.3\ \text{s K}\) seems to explain satisfactorily most of the data for the different compositions. A deviation which is just outside experimental error is observed for \(x = 0.1\) in the temperature range 100-250 K and is not presently understood. The larger estimated error in the data for \(x = 0.5\) is due to the difficulty in performing measurements on an inhomogeneously broadened NMR line (see Chapter 2). It should be noted that the independence of the \((T_1 T)\) product from \(x\) and from temperature is consistent with the Knight shift results if the Korringa relation \[70\] holds.
Figure 3.49: The variation of the spin-lattice relaxation rate $T_1^{-1}$ as a function of temperature $T$ for the metallic samples in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$, with $x \leq 0.6$
CHAPTER 4. QUANTITATIVE ANALYSIS OF THE $^{51}\text{V}$ NMR AND SUSCEPTIBILITY RESULTS FOR THE METALLIC PHASE

In this chapter, the magnetic susceptibility data and the NMR data are analyzed together in order to obtain quantitative information about the density of electronic states, the enhancement effects due to electronic interactions and about the hyperfine interactions.

The magnetic susceptibility $\chi$ can be partitioned in the following manner:

$$\chi_{\text{meas}} = \chi_{\text{Pauli}} + \chi_{\text{Landau}} + \chi_{\text{core}} + \chi_{\text{VV}}$$

(4.1)

The first term is the spin contribution due to itinerant carriers. $\chi_{\text{core}}$ is the (orbital) diamagnetism due to the ion cores and $\chi_{\text{VV}}$ is the (orbital) Van Vleck contribution. The (orbital) Landau contribution from the itinerant carriers is given by

$$\chi_{\text{Landau}} = -\frac{1}{3}(m_e/m^*)^2 \chi_{\text{Pauli}} (1 - \alpha)$$

(4.2)

and is negligible here since the effective mass $m^*$ is significantly greater than the free electron mass and the Stoner enhancement factor $1/(1-\alpha) \gg 1$. In particular, for an effective mass ratio $m^*/m_e = 4$ and a Stoner enhancement factor $1/(1-\alpha) = 4$, (see end of this chapter for the origin of these values) the Landau contribution is only 0.5% of the Pauli susceptibility. The contribution to the core diamagnetism by the various ions is: $\chi_{\text{core}}(\text{La}^{3+}) = -0.20$, $\chi_{\text{core}}(\text{Sr}^{2+}) = -0.15$, $\chi_{\text{core}}(\text{V}^{3+}) = -0.10$. 


\( \chi_{\text{core}}(V^{1+}) = -0.07 \) and \( \chi_{\text{core}}(O^{2-}) = -0.12 \) in units of \( 10^{-4} \text{ cm}^3/\text{mole} \) [67]. Thus, by subtracting the total \( \chi_{\text{core}} \) from the experimental data one is left with

\[
\chi = \chi_{\text{Pauli}} + \chi_{VV},
\]

(4.3)

(\text{where } \chi = \chi_{\text{meas}} - \chi_{\text{core}}) which is the relevant quantity to be analyzed in connection with the NMR data.

The main features that should be explained are: the large temperature independent susceptibility; the increase of the susceptibility with increasing lanthanum doping (for \( x < 0.7 \)); the composition independent positive Knight shift and the Korringa-like behaviour of \( T_1^{-1} \).

The set of equations adopted to fit the experimental results [68] are:

\[
\chi = \chi_d + \chi_s + \chi_{VV}
\]

(4.4)

\[
\mu_B K = \chi_d H_{hf,d} + \chi_s H_{hf,s} + \chi_{VV} H_{hf,\text{orb}}
\]

(4.5)

\[
S(T_1 T)^{-1} = \beta_d K_d^2 R_d + \beta_s K_s^2 + (\mu_B D_d(\epsilon_f) H_{hf,\text{orb}})^2 R_{\text{orb}}
\]

(4.6)

In equation 4.4, the term \( \chi_{\text{Pauli}} \) of equation 4.3 is partitioned into a spin contribution due to d-electrons \( \chi_d \) and a spin contribution due to carriers with an s (and/or p) character \( \chi_s \). There are thus three contributions to \( \chi \) when \( \chi_{VV} \) is included. Likewise, the Knight shift \( \chi \) in equation 4.5 has been written as a sum of three terms containing the corresponding hyperfine fields. In equation 4.6 for the relaxation rate, we have assumed a Korringa relationship for d and s electrons with corresponding enhancement factors \( \beta_d \) and \( \beta_s \); the orbital contribution is related directly to the density of d-electron states at the Fermi level, \( D_d(\epsilon_f) \) and \( R_d \) and \( R_{\text{orb}} \) are reduction factors arising from orbital degeneracy which have both been assumed to be 0.3 for
vanadium d electrons [69]. In Eq. 4.6 the constant $S = \frac{\gamma_e}{\gamma_n} \frac{2h}{4\pi k_B}$ is $3.74 \times 10^{-6}$ sec-K for the $^{51}V$ nucleus.

We proceed now to estimate the hyperfine fields in equations 4.5 and 4.6. We assume $H_{hf,d} = -125$ kG/$\mu_B$ which pertains to an unpaired atomic 3d-electron. The above value is close to the one (-117 kG/$\mu_B$) used to interpret the Knight shift data in vanadium metal [70] and is intermediate between the values used to fit the data in metallic VO$_2$ ($V^{1+}$, $H_{hf,d} = -85$ kG/$\mu_B$) [71] and V$_2$O$_3$ ($V^{3+}$, $H_{hf,d} = -140$ kG/$\mu_B$) [72]. For the orbital term we assume $H_{hf,orb} = 410$ kG/$\mu_B$ which is intermediate between the values used in VO$_2$ ($H_{hf,orb} = 455$ kG/$\mu_B$, [71]) and V$_2$O$_3$ ($H_{hf,orb} = 395$ kG/$\mu_B$, [72]). For the s-contact term we take $H_{hf,s} = 1100$ kG/$\mu_B$ which corresponds to the vanadium atomic hyperfine field reduced by a factor of 0.7 as for vanadium metal [69]. The equations 4.5 and 4.6 can now be rewritten as:

$$K' = -0.23 \chi_d + 1.97 \chi_s + 0.73 \chi V$$ (4.7)

$$(T^2 T)^{-1} = 0.40 \beta_d \chi_d^2 + 104 \beta_s \chi_s^2 + 0.45 D_d^2(\epsilon_f)$$ (4.8)

where $\chi$ is in $10^{-4}$ cm$^3$/mole, $K'$ in % and $D_d(\epsilon_f)$ in states/eV-vanadium atom.

From equations 4.4, 4.7, and 4.8, one can try to partition the susceptibility into its three components. However, since no temperature dependence of either $\chi$ or $K'$ is observed experimentally in the metallic phase, one has to make further assumptions to reduce the number of fitting parameters. Equation 4.8 puts a constraint on the maximum value that $\chi_s$ can have for a given relaxation rate by setting $\chi_d = 0$ and $D_d(\epsilon_f) = 0$. For our case this is approximately $0.16 \times 10^{-4}$ cm$^3$/mole. In view of the large value of the measured susceptibility, $\chi_s$ can be neglected in equation 4.1.
although not necessarily in equations 4.7 and 4.8.

From equations 4.4 and 4.7 and using the experimental values for $\chi$ and $K$, we derive the $\chi_d$ and $\chi V V$ contributions shown in Figure 4.1, for three different values of $\chi_s$. The partitioning of $\chi$ into $\chi_d$ and $\chi V V$ (plus $\chi_s$) is not very sensitive to the value assumed for $\chi_s$ as shown in Figure 4.1, where the values obtained by assuming $\chi_s = 0, 0.10$ and $0.15 \times 10^{-4}$ cm$^3$/mole are plotted.

We turn now to equation 4.8 for the relaxation rate. If we write $\chi_d = D_d(\epsilon_f)/3.09(1 - \alpha)$ (in the units of equation 4.8) as is customary and assume $\beta_d = 1 - \alpha$ [68] and $\beta_s = 1$, then from equation 4.8 one has

$$\frac{1}{T(T)} = 0.04D_d^2(\epsilon_f)/(1 - \alpha) + 104\chi_s^2 + 0.45D_d^2(\epsilon_f) \tag{4.9}$$

where the d-spin susceptibility is exchange enhanced by a Stoner factor $1/(1 - \alpha)$ with respect to the band structure Pauli susceptibility (the enhancement effects which can be described in terms of a band structure effective mass are included in $D_d(\epsilon_f)$). The values obtained for $D_d(\epsilon_f)$ and $1/(1 - \alpha)$ which fit equations 4.4, 4.7, and 4.8 are plotted in Figure 4.2 and Figure 4.3 for the three values of $\chi_s$. We have not attempted to assume any variation of $\chi_s$ with the lanthanum doping concentration.

An almost constant $D_d(\epsilon_f)$ and an increase in the susceptibility due to an increase $1/(1 - \alpha)$ (as a function of La concentration), as deduced in Figure 4.2 and Figure 4.3, seems to be necessary to explain the nuclear relaxation data. However, no unambiguous partition between the two effects is possible because these results are too sensitive to the value and composition independence assumed for the s-spin susceptibility $\chi_s$. Low temperature specific heat data, from which $D_d(\epsilon_f)$ can be inferred, should allow to clarify this point.

In contrast to $D_d(\epsilon_f)$ and $1/(1 - \alpha)$ above, the values of $\chi_d$ and $\chi V V$ are not
Figure 4.1: The d-spin $\chi_d$ and the Van Vleck $\chi_{VV}$ susceptibilities as a function of composition $x$, for different assumed values of $\chi_s$, from a combined analysis of the NMR and the susceptibility data for $La_xSr_{1-x}VO_3$. 
Figure 4.2: The d-band density of states at the Fermi level $D_{d}(\epsilon_f)$ as a function of the La doping level $x$, for different assumed values of $\chi_s$, for $La_xSr_{1-x}VO_3$. 
Figure 4.3: The Stoner exchange enhancement $1/(1 - \alpha)$ as a function of the La doping level $x$, for different assumed values of $\chi_s$, for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$. 
sensitive to the choice of $\chi$, and are considered reliable within our model. Our values obtained here for the Van Vleck susceptibility, $\chi_{VV} \sim 0.5-1.8 \times 10^{-4}$ cm$^3$/mole V from Figure 4.1, are intermediate between the values of $\chi_{VV}$ for metallic VO$_2$ ($V^{4+}$, $\chi_{VV} = 0.65 \times 10^{-4}$ cm$^3$/mole V) [71] and V$_2$O$_3$ ($V^{3+}$, $\chi_{VV} = 2.10 \times 10^{-4}$ cm$^3$/mole V) [72]. The density of states, in a band theory approach, is given by

$$D_d(\epsilon_f) = (V_{cell}/2\pi^2)(2m^*/h^2)(3\pi^2 N/V_{cell})^{1/3} \times 1.6 \times 10^{-12}$$

(4.10)

where $D_d(\epsilon_f)$ is the density of states in units of equation 4.8, $V_{cell}$ is the volume of a unit cell in cm$^3$, $m^*$ the band effective mass in g and $N$ the number of carriers per unit cell (h is in cgs units). For the case of lanthanum doping $x = 0.1$, taking $a_0 = 3.9 \text{ Å}$, $N = 0.9$ and $D_d(\epsilon_f) \sim 2$ (see Figure 4.2), we get the (band) effective mass ratio $m^*/m_e \sim 4$. 
CHAPTER 5. CONCLUSIONS

We find complete solid solubility in the La$_x$Sr$_{1-x}$VO$_3$ system for $0 \leq x \leq 1$. There is a composition induced cubic to tetragonal transition with increasing $x$ at $x \approx 0.7$. Some samples in the region $x < 0.7$ were found to have tetragonal/orthorhombic distortions from cubic symmetry.

The transition from a metallic strongly exchange enhanced Pauli paramagnet to an antiferromagnetic insulator occurs in the vicinity of $x = 0.8$. The susceptibility (at room temperature) was found to be rather smoothly varying with $x$ and devoid of any discontinuity or jump in the vicinity of the metal to insulator transition. This is akin to the situation in La$_{2-x}$Sr$_x$CuO$_4$ where the parent antiferromagnet (La$_2$CuO$_4$) gradually gives way (in terms of the susceptibility) to superconductivity. Moreover, in the normal metallic state of this superconductor, antiferromagnetic spin fluctuations are found to persist. The magnetic susceptibility for the metallic samples (in La$_x$Sr$_{1-x}$VO$_3$) is temperature independent. Analysis of the susceptibility data in conjunction with the results of $^{51}$V NMR (for La$_x$Sr$_{1-x}$VO$_3$) indicates that the susceptibility shows a strong enhancement which appears to be comprised of an exchange enhancement of the Stoner type and also an effective mass enhancement due to band structure effects. We find a density of states at the Fermi level to be about 2 states/eV-formula unit which is about four times the value one would
get in the free electron approximation (≈ 0.5 states/eV-FU). The effective mass is approximately constant in the metallic region and the increase in the susceptibility on going towards the metal to semiconductor transition appears to be due to a Stoner type of enhancement. It should be mentioned that the values of the density-of-states at the Fermi level and of the Stoner enhancement factor are sensitive to the presence of a term in the susceptibility which comes from a fractional s character to the carriers. This appears to be a system where a ferromagnetic exchange enhancement and narrow d-band correlations coexist in the metallic phase and the metal to semiconductor transition is accompanied by the localization of the V d-electron magnetic moment on the V atoms. The antiferromagnetic interactions determine the properties of the insulating phase. No evidence was found from NMR T^{-1} measurements for an enhancement of the staggered susceptibility at q = q_{AF} for the metallic samples even close (x = 0.6) to the antiferromagnetic insulating phase. Also, the Knight shift and the susceptibility are independent of temperature for these samples near the metal-insulator transition. We do not find evidence for antiferromagnetic spin fluctuations for the metallic samples in our system.

Many properties of the system studied appear to be quite similar to those of the high-Tc cuprate superconductors including the phase diagram as a function of Sr concentration. What might possibly be different is the large exchange enhancement present in vanadium based system and not observed, for example, in La_{2-x}Sr_{x}CuO_{4}. This enhancement of the uniform susceptibility persists up to the metal-insulator transition and only when the V d-electrons become localized does the dominant interaction becomes antiferromagnetic. In the La_{2-x}Sr_{x}CuO_{4} system on the other hand, even in the metallic phase (where the carriers are itinerant) there is evidence
of antiferromagnetic spin correlations.

For La$_{0.9}$Sr$_{0.1}$VO$_3$ we found two anomalies in the susceptibility as a function of temperature. The high temperature anomaly corresponds to antiferromagnetic ordering whereas the low temperature anomaly appears to be associated with onset of canting due to the double exchange mechanism. The enhancement of susceptibility in the metallic samples due to ferromagnetic exchange enhancement and presence of ferromagnetic double exchange in the antiferromagnetically ordered sample, then, seem to complement each other.

The compound LaVO$_3$ is found to be a tetragonal distortion of the cubic perovskite structure at room temperature. In low temperature x-ray diffraction measurements we were unable to detect any change in the crystal structure in the vicinity of the Néel temperature.

We have observed a negative magnetic moment (in low fields) for LaVO$_3$ in field-cooled experiments. Also seen is hysteresis in M(H) isotherms below the Néel temperature, for ZFC as well as FC cases. The diamagnetism (as well as the weak ferromagnetism) appears to be related to ferrimagnetism in this compound which arises due to the presence of magnetically inequivalent vanadium sites leading to an incomplete cancellation of the magnetization of the two sublattices. The following is a possible explanation for the effects observed in LaVO$_3$. The diamagnetism is perhaps due to different temperature dependences of the sublattice magnetizations. Near (and below) $T_N$ the two sublattices align ferrimagnetically, and in the case of a FC experiment, with the weak ferromagnetic moment along the direction of the applied field but due to different temperature dependences of the sublattice magnetizations (and the inability of the spins to rotate, due to anisotropy) the net moment changes
sign and is then aligned opposite to the applied field, at lower temperatures. If the sample is cooled a field which is high enough (to overcome the anisotropy energy) then the net moment is always parallel to the applied field. The diamagnetism does not appear to be related to superconductivity and appears to be due to ferrimagnetism.

We have observed $^{51}$V NMR by the CW method and the NMR measurements confirm the association of the peak in the susceptibility with magnetic ordering. An additional broad signal with a positive shift was observed by the pulse method, which could be due to a small amount of impurity or due to the presence of V$^{4+}$ holes (due to the fact that the oxygen content is slightly greater than 3).
BIBLIOGRAPHY


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