Orbital, charge and magnetic order of RVO3 perovskites
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CHAPTER 4

Insulator-to-Metal transition in (R,Ca)VO$_3$

4.1 Introduction

The metal-insulator transition (MIT) in transition metal oxides due to electron correlation effects has been widely studied as many anomalous properties are exhibited through the transition. Still, a better comprehension needs to be achieved regarding the MIT. At first sight, the concept of a transition from an insulator to a metal may seem to involve a trivial change in resistivity, but it is actually very difficult to comprehend all the electronic interactions. As mentioned in Chapter 1, RVO$_3$ compounds are defined as Mott insulators in the broad sense of the definition and more precisely as Mott-Hubbard insulators in the ZSA classification scheme [1]. The metal-insulator transition can be achieved easily by band filling control, i.e. via substitution of divalent cations (e.g. Ca, Sr) on the rare-earth site. This changes an equivalent number of V$^{3+}$ to V$^{4+}$, resulting in changes in the filling of the 3$d$ band.

In connection with the previous chapter, one may wonder what happens to the orbital ordering (OO) with hole doping. From general considerations we expect that the OO is incompatible with a metallic state. For example, in La$_{1-x}$Sr$_x$VO$_3$ it has been reported that the G-type OO melts at the transition from insulator to metal ($x_c \approx 0.2$) [2]. This result indicates that hole doping induces the melting of the OO. A recent report has demonstrated that this may in fact not be the case [3].
Fujioka et al. have reported results (based essentially on specific heat experiments) on the behavior of the OO upon hole doping and its relation to the MIT. Their study shows that apart from La$_{1-x}$Sr$_x$VO$_3$, other doped vanadates clearly indicate orbital disordering at $x_o \approx 10$-$20\%$, a doping level well below the $x_c$ of the MIT, and it is argued that the hole motion alone does not cause the collapse of the G-type OO phase which would be more related to quenched disorder arising from the solid solution of a small trivalent and large divalent cation. This phenomenon has also been reported for manganese perovskites [4, 5]. C-type OO seems to be much less stable with respect to doping and disappears with just 2% Ca in Y$_{1-x}$Ca$_x$VO$_3$. In another report, Ishihara predicts that the motion of the doped hole reduces the spin order parameter which in turn causes a softening of orbitons leading to the instability of the G-type OO and C-type OO [6]. The phenomenon is explained differently by Khaliullin [7]. He shows that his model with fluctuating orbitals can also apply to doped holes because of orbital-charge separation and that even if the hole-motion is not frustrated by G- or C-type OO, it is frustrated in the spin-G phase in all directions, thus explaining why the C-type OO is less stable than the G-type OO phase with respect to doping.

Although reports concerning OO and the MIT are recent, the process of achieving the MIT in the vanadates by band filling control can be traced back to the 1970’s and again after the discovery of high-temperature superconductivity in cuprates with perovskite-related structures. Three systems have consistently been investigated: (La,Sr)VO$_3$ [2, 8–14], (La,Ca)VO$_3$ [15–18] and (Y,Ca)VO$_3$ [19–26]. The main differences between these systems were found in the range in which solid solutions could be achieved and which crystal structure is adopted. In Ca-doped LaVO$_3$ and YVO$_3$ all reports find a continuous solid solution over the whole doping range. Transitions from an antiferromagnetic insulator to an antiferromagnetic metal (at $x_c=0.2$), then to a paramagnetic metal take place for (La,Sr)VO$_3$. The resistivity displays a $T^{1.5}$ dependence in the vicinity of the MIT which is ascribed to strong antiferromagnetic spin fluctuations [2, 14]. The same temperature dependence of the resistivity is observed for (La,Ca)VO$_3$ ($x_c \approx 0.26$) [17]. However it should be noted that Nguyen and Goodenough report a divergence in the magnetic susceptibility for concentrations $>x_c$, ascribed to a spin-blocking temperature [16]. For these compounds evidence of variable range hopping has been reported by most authors which would indicate an Anderson transition. An upturn of the resistivity at low-temperatures has also been observed, indicating disorder in the system. In (Y,Ca)VO$_3$, the transition is found to appear at considerably higher doping levels ($x_c \approx 0.5$). Although there are several reports on this system, there are some major differences observed in the magnetization data,
and no careful structural and transport investigation has been carried out. We thus initiated the study of the MIT in Ca-doped YVO$_3$ as well as in SmVO$_3$ and PrVO$_3$. We carried out a careful investigation of the structural, magnetic and transport properties in order to study the nature of the MIT in these compounds.

4.2 Experimental results

4.2.1 Structural evidence

The RVO$_3$ compounds (R = Y, Pr, Sm) are known to crystallize in the orthorhombic perovskite structure [27–30] at room temperature (RT) and ambient pressure. We studied the RT crystal structure of R$_{1-x}$Ca$_x$VO$_3$ (R = Y, Sm, Pr), using X-Ray diffraction and obtained in each case the lattice parameters as a function of $x$ (Apdx. A.1). From this we calculated the unit cell volume (Fig. 4.1). The volume of stoichiometric CaVO$_3$ [31] has also been included in these plots. This gives a broader view of the evolution of the unit cell parameters with increasing calcium concentration until full substitution of the trivalent rare earth by divalent calcium is reached.

There is a continuous change in the lattice parameters with increasing calcium content. First, the lattice parameters $a$ and $b$ become more and more similar with increasing calcium concentration (Fig. 4.2). Second, the value of the $c/a$ ratio (Fig. 4.3) decreases toward $\sqrt{2}$ with increasing calcium concentration. This implies that the orthorhombic distortion decreases with increasing calcium concentration in each series. The same holds for increasing rare earth radius. In the case of Pr$_{1-x}$Ca$_x$VO$_3$, the difference between $a$ and $b$ is small as it has one of the least distorted structures. Although $b$ is always greater than $a$, the ratio $c/a$ is extremely close to $\sqrt{2}$ (especially for $x=0.6$). There is a slight discontinuity or change of slope in the volume near $x=0.25$ for Pr$_{1-x}$Ca$_x$VO$_3$, $x=0.15$ for Sm$_{1-x}$Ca$_x$VO$_3$, and $x=0.25$ for Y$_{1-x}$Ca$_x$VO$_3$ (Fig. 4.1). Although this change of slope is not as striking a proof for the MIT as the structural change is in the case of La$_{1-x}$Sr$_x$VO$_3$ (where there is a symmetry change from orthorhombic to rhombohedral [32]), it still coincides with a change in the properties of the compounds as will be discussed in the following sections.

We also studied the octahedral tilt angle as a function of doping. Its value is difficult to determine accurately with a laboratory diffractometer. Nevertheless, we were able to follow the trend of the tilt angle with increasing calcium doping shown in Figure 4.4. We have added the values of the parent compounds in each case, which were extracted from synchrotron radiation measurements. The
octahedral tilt angle $\phi = 180 - \theta$ decreases with increasing calcium concentration, implying an increasing bandwidth [3]. For $R = \text{Pr}$, the tilt angle could not be determined from our data for all compositions.

Figure 4.1: Unit-cell volume for $R_{1-x}Ca_xVO_3$ with $R =$ Y, Sm, Pr, La).

Figure 4.2: Evolution of the $b/a$ ratio with increasing calcium concentration.

Figure 4.3: Evolution of the $c/\sqrt{2}a$ ratio with increasing calcium concentration.

Figure 4.4: Evolution of the octahedral tilt angle $\phi$ with increasing calcium concentration.

4.2.2 Magnetic properties

4.2.2.1 Magnetic properties of $Y_{1-x}Ca_xVO_3$

The magnetic behavior of the parent compound, YVO$_3$, has been widely studied by various techniques both on single- and poly-crystalline samples [33–39].
In recent years, agreement has been reached on its magnetic behavior: YVO$_3$ presents two magnetic phase transitions, the first at 114K and the second at 77K. Below the onset of magnetic ordering, the sample displays an antiferromagnetic ordering in the $ab$-plane and a ferromagnetic ordering along the $c$-axis (C-type), whereas below the second transition, the sample is antiferromagnetic in all directions (G-type). A small canting of the spins gives rise to a weak ferromagnetic moment.

First of all, attention should be paid to the field dependence of the magnetization in Y$_{0.9}$Ca$_{0.1}$VO$_3$ [21, 26]. The field-cooled measurement shows that around and below the Néel temperature ($T_N$), increasing the magnetic field decreases the susceptibility of the compound (Fig. 4.5). This was previously explained [21] as an anomalous saturation or a field induced diamagnetic susceptibility and has also been observed for YVO$_3$ [35]. It should also be noted that this field dependence is suppressed above 5000 Oe (Fig. 4.5). Indeed, one can see that the magnitude of the ferromagnetic-like component around $T_N$ decreases tremendously when performing the measurement in 5000 Oe compared to 1000 Oe, but there is little change when increasing further to 10000 Oe. We conclude that the ferromagnetic contribution is dominant in low magnetic fields whereas the antiferromagnetic contribution is dominant in high magnetic fields. This concurs with the expectation that the ferromagnetic component saturates with increasing field, whereas the antiferromagnetic component increases linearly with field.

Our measurements of the magnetization of Y$_{1-x}$Ca$_x$VO$_3$ show that in the paramagnetic region, we can fit the data with a Curie-Weiss behavior (including a temperature independent term [TIP]), and we present in the insert of Figure 4.6 the difference between the expected values of the paramagnetic effective moment and those obtained experimentally. We observe that the experimental values are slightly lower than the calculated ones, becoming much lower when reaching 50% calcium doping. Our values are comparable to those found in other reports [24,25].

A deviation from the Curie-Weiss behavior due to short-range ordering of the spins has been observed above $T_N$ in YVO$_3$ [35] and is still present just above $T_N$ in the doped material (below $T=120$K), although it appears closer to $T_N$ than in the parent compound (below $T=130$K). On cooling through $T_N$, the magnetization shows that the canted-spin ferromagnetism is oriented in the direction of the field, and that it has the same complex temperature dependence as its parent compound [35,39]. However, these magnetization measurements on pressed pellets do not allow us to attribute the anomalies that can be seen in the low temperature range to a second magnetic phase transition as in YVO$_3$ [39].

The value of $T_N$ surprisingly decreases only very slightly with increasing cal-
cium doping. Previous studies of Ca-doped and Sr-doped rare-earth vanadates have reported that $T_N$ decreases substantially with increasing doping concentration [10, 13, 15, 40]. Despite the fact that $T_N$ changes little, the magnitude of the ferromagnetic-like anomaly decreases quite sharply with increasing calcium doping.

If we compare our experimental data with those in the literature, we see that two different kinds of magnetization results exist. Two reports [21, 26] present similar data to us as can be seen in Figure 4.7. However, in a second group of reports [3, 23–25] the Néel temperature is shown to decrease sharply above 20% calcium doping, reaches a value of approximately 20K between 40 and 60% of calcium doping, and vanishes above this concentration. However, very few susceptibility curves are shown in these reports which makes it difficult to draw a fair comparison. Only Fujioka et al. [3] present experimental data, and only for very low doping concentrations. Regarding the curve representing 30% calcium concentration, no anomaly at $T_N$ can be resolved from the data presented (reproduced in Fig. 4.8) and the authors conclude that $T_N$ is at much lower temperature. However, our experimental results, as well as those reported by others [21], clearly show a large decrease of the magnitude of the ferromagnetic component with increasing calcium concentration, which could account for the lack of an obvious anomaly in Figure 4.8. Weighing all the available experimental evidence, it appears to us that $T_N$ decreases only slightly for $x<0.5$. 

Figure 4.5: Comparison of the field-cooled magnetization for different magnetic fields in $Y_{0.9}Ca_{0.1}VO_3$.

Figure 4.6: Temperature dependence of the field-cooled susceptibility in $Y_{1-x}Ca_xVO_3$, $H=1000$ Oe.
4.2. Experimental results

4.2.2.2 Magnetic properties of Sm$_{1-x}$Ca$_x$VO$_3$

The magnetic susceptibility of the Sm$_{1-x}$Ca$_x$VO$_3$ compounds (Fig. 4.9) is less complex than that of the Y-series. $T_N$ decreases smoothly with increasing calcium concentration from 130K for $x=0$ to 100K for $x=0.40$. It is not possible to detect any signature of magnetic ordering in the compound with $x=0.50$ for which the susceptibility can be fitted with Curie-Weiss behavior at all temperatures. Only the parent compound shows additional features that are suppressed by chemical or external pressure [29, 41].

The susceptibility curves above the magnetic ordering temperature can be well fitted with a Curie-Weiss behavior, and the resulting values of the paramagnetic effective moment are shown in the insert of Figure 4.9. The calculation of the paramagnetic effective moment incorporates the rare-earth concentration and the valence change of the vanadium [42]. As the calcium concentration increases, the
difference between the experimental and calculated values becomes larger, and the moment measured for $x=0.50$ is very small. A similar trend is observed in $Y_{1-x}Ca_xVO_3$. However, in $Sm_{1-x}Ca_xVO_3$, the difference between the experimental and expected values for high $x$ is much larger than in $Y_{1-x}Ca_xVO_3$, and may be explained by the presence of the non-magnetic Sm$^{2+}$ cation in the sample as will be more extensively explained in Paragraph 4.2.3.2c.

![Figure 4.9: Temperature dependence of the field-cooled susceptibility in $Sm_{1-x}Ca_xVO_3$, H=1000 Oe.](image)

In Figure 4.10 we show the magnetic field dependence of the magnetization at 5K. The data show a large coercive field and a large asymmetry between the positive and negative fields for the parent and $x=0.10$ compounds. Although the asymmetry could come from the fact that the samples were pressed powder pellets, we have no specific explanation of its origin. With increasing calcium concentration the magnitude of the coercive field decreases until it vanishes for high concentration. The value of the magnetization decreases with increasing calcium doping, which is expected as the compounds become paramagnetic. The remanent magnetization can be extracted for each composition and its value decreases with increasing calcium concentration (Fig. 4.11).
4.2. Experimental results

4.2.2.3 Magnetic properties of Pr$_{1-x}$Ca$_x$VO$_3$

Measurements in different magnetic fields (Fig. 4.12) show a magnetic susceptibility behavior similar to that observed in Y$_{1-x}$Ca$_x$VO$_3$ (Fig. 4.5)(even if the low-temperature behavior is less complex). Also in this compound, the ferromagnetic contribution is dominant in low magnetic fields and the antiferromagnetic contribution is dominant in high magnetic fields.

The susceptibility data for Pr$_{1-x}$Ca$_x$VO$_3$ show the ordering of the vanadium spins at $T_N$. Below $T_N$ (Fig. 4.13), a large decrease of the low-temperature susceptibility is observed between $0.10 \leq x \leq 0.15$ and between $0.30 \leq x \leq 0.40$.

The decrease of $T_N$ with increasing calcium concentration seems more pronounced than in the Y and Sm series. However, due to the presence of the paramagnetic moment of Pr$^{3+}$, $T_N$ cannot be extracted accurately. This will not affect the discussion of the nature of the MIT in this series. The compound with $x=0.60$ does not show any kind of antiferromagnetic ordering anomaly down to the lowest temperatures and follows Curie-Weiss behavior above 10K, where the Pr spins begin to fully order. Results from another report [3] show the behavior of $T_N$ with increasing doping concentration up to $x=0.30$ in single crystals. Our values are very similar.
Figure 4.12:
Comparison of the field-cooled magnetization for different magnetic fields in Pr_{0.6}Ca_{0.4}VO_{3}.

Figure 4.13:
Temperature dependence of the field-cooled susceptibility in Pr_{1-x}Ca_{x}VO_{3}, H=1000 Oe.

Above T_N the paramagnetic susceptibility was fitted with a Curie-Weiss function, and the values of $p_{\text{eff}}$ extracted. For high calcium concentration, $p_{\text{eff}}$ does not deviate as strongly from the calculated values as in the Y and Sm series. This may be due to the strong contribution of the praseodymium.

The Pr^{3+} spins show a large ferromagnetic component, but their ordering temperature is difficult to define from the susceptibility curves as they experience the effective field of the vanadium spins and might begin to order shortly below T_N. The ferromagnetic coupling of the Pr^{3+} spins can clearly be seen from the hysteresis curve at 5K (Fig. 4.14). The coercive field at this temperature is symmetric with applied field and its value remains constant with increasing calcium concentration. The remanent magnetization (Fig. 4.15) decreases linearly with increasing calcium concentration. It would thus seem that at 5K, it is the ferromagnetic coupling of the Pr^{3+} spins that is mainly observed and that the signal has little contribution from the V^{3+} spins.
4.2. Experimental results

4.2.3 Transport properties

4.2.3.1 Transport properties of $Y_{1-x}Ca_xVO_3$

a. Resistivity

From the resistivity measurements performed on the $Y_{1-x}Ca_xVO_3$ samples (Fig. 4.16), information relevant to the type of conduction can be extracted. The measurable temperature range increases with increasing calcium doping as the sample becomes more conducting.

The $x=0.10$ sample shows a thermally activated behavior:

$$\rho = \rho_0 e^{\frac{E_a}{k_B T}}$$  \hspace{1cm} (4.1)

and an activation energy of $E_a=0.124$ eV is extracted, which is comparable to a published report by Kasuya et al. [20].

The $x=0.20$ and $x=0.30$ samples behave slightly differently: although they present a thermally activated behavior, the low-temperature region variable range hopping which is defined by:

$$\rho = \rho_0 e^{\frac{T_0}{T}}^{1/4}$$  \hspace{1cm} (4.2)

$T_0$ being a parameter related to the density of localized states at the Fermi level $N(E_F)$ by the following equation:

$$T_0 = \frac{24\alpha^3}{\pi N(E_F)k_B}$$  \hspace{1cm} (4.3)
From $T_0$ and using a reasonable value for $\alpha$ (the fall-off rate of the envelope of the wave function) [43], we can extract $N(E_F)$ and obtain values of $3.36 \times 10^{18}$ and $1.2 \times 10^{19}$ cm$^{-3}$eV$^{-1}$ for $x=0.2$ and $0.3$, respectively. These values are consistent with what is expected: the density of localized states at the Fermi level increases by almost one order of magnitude between the two compositions.

Maiti et al. [44] reported that in the case of La$_{1-x}$Ca$_x$VO$_3$, the temperature dependence of the resistivity can be fitted over the entire temperature range using simultaneously thermally activated and variable range hopping behaviours. We find that in the case of Y$_{1-x}$Ca$_x$VO$_3$, both contribute independently to the resistivity depending on the temperature range.

As can be seen in Table 4.1, the activation energy decreases only slightly from $x=0.1$ to $x=0.20$, but then significantly for $x=0.30$. This is in disagreement with the previously mentioned report [20] where the activation energy hardly changes up to $x=0.40$. A report by Kawanaka et al. [25] presents similar data to ours in the case of $x=0.30$ and also a large decrease between the $x=0.30$ and $x=0.40$ compounds, which relates better to our report. However, their extracted value of the activated energy (0.2 eV) is extremely high. A more recent report by Cintolesi et al. [26] presents activation energy values that are slightly lower than our values, but with a similar doping dependence.
4.2. Experimental results

\[
x = \begin{array}{|c|c|c|c|c|}
\hline
E_a & \rho_01 & \rho_02 & T_0 \\
\text{(eV)} & \text{(Ω.cm)} & \text{(Ω.cm)} & \text{(K)} \\
\hline
0.1 & 0.124 & 0.045 & \text{E1} \\
0.2 & 0.106 & 0.0038 & 1.63 \times 10^{-14} & 2.11E8 \\
0.3 & 0.064 & 0.0032 & 7.48 \times 10^{-12} & 5.93E7 \\
\hline
\end{array}
\]

Table 4.1: Fitting parameters for the temperature dependence of the resistivity in \( Y_{1-x}Ca_xVO_3 \). \( E_a \) and \( \rho_01 \) are the activation energy and the prefactor in the thermally activated behavior function, respectively; \( \rho_02 \) and \( T_0 \) are the residual resistivity and the extracted temperature for the variable range hopping function respectively.

When the calcium concentration increases further, the resistivity decreases with decreasing temperature as is expected for a metallic sample and can be fitted by the following equation:

\[
\rho = \rho_{03} + a_{e-ph}T + a_{e-e}T^2
\]

where \( \rho_{03} \) is the residual resistivity, \( a_{e-ph} \) is the electron-phonon scattering and \( a_{e-e} \) is the electron-electron interaction. There is an upturn in the low-temperature dependence of the resistivity for \( x=0.4 \), in agreement with the report by Nishihara et al. [24]. The report presented by Cintolesi et al. [26] shows a fully metallic behavior, although the authors report that at very low temperature the linear behavior is discontinued. Such an upturn of the resistivity at low temperature has been widely observed [45–47] and corresponds to a \( \sqrt{T} \) dependence of the conductivity. Its origin will be discussed in the following Section. Indeed, the conductivity of our sample strictly follows this \( \sqrt{T} \) dependence below 40K with:

\[
\sigma = 7.96 + 29.47\sqrt{T}.
\]

Above 165K, we observe a typical Fermi-liquid behavior, which is a function \( T^2 \) (Table 4.2). In the intermediate temperature region, the \( T \) dependence of the electron-phonon scattering is combined with that of the \( T^{-0.5} \) dependence.

For \( x=0.50 \), the resistivity decreases with decreasing temperature and the data can be fitted by a Fermi liquid behavior over the entire temperature range.
Table 4.2: Fitting parameters for the temperature dependence of the resistivity in Y$_{1-x}$Ca$_x$VO$_3$: $\rho_{03}$, $a_{e-ph}$ and $a_{e-e}$ are the residual resistivity, the electron-phonon scattering and the electron-electron interaction respectively.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\rho_{03}$ ($\Omega \cdot cm$)</th>
<th>$a_{e-ph}$ ($\Omega \cdot cm \cdot K^{-1}$)</th>
<th>$a_{e-e}$ ($\Omega \cdot cm \cdot K^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 ($T \geq 170K$)</td>
<td>0.0021</td>
<td>0</td>
<td>3.138E-8</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0014</td>
<td>1.03E-6</td>
<td>1.82E-8</td>
</tr>
</tbody>
</table>

b. Seebeck effect

From the Seebeck measurements presented in Figure 4.17, two distinct behaviors can be observed below and above $x=0.30$. In the low concentration range, the Seebeck coefficient has a thermally activated behavior defined by:

$$S = \frac{k_B}{e} \cdot \frac{E_a}{k_B T}$$

(4.5)

where $k_B$ is Boltzmann’s constant and $e$ the elementary unit of charge. We thus performed the corresponding fit to extract the activation energy $E_a$ for these two compounds. Regarding the $x=0.10$ sample, extracting the data down to 85K (where the Seebeck coefficient presents a large upturn), we find $E_a=0.0076$ eV, which is smaller than the activation energy extracted from the resistivity measurement ($0.124$ eV, Table 4.1). This indicates small-polaron conduction of mobile charge carriers [40]. The statistical contribution of the small-polaron to the Seebeck coefficient is defined as:

$$S = \frac{k}{q} \cdot ln\left[\frac{\beta(1-c)}{c}\right]$$

(4.6)

In our system, $c$ is the fraction of vanadium sites occupied by mobile holes, and $\beta$ is the spin-degeneracy term ($\beta = 2$); we calculate $S=251\mu V/K$ for $x=0.10$. Below 70K, the mobile charge carriers are frozen out.

For $x=0.20$, we find $E_a=0.0034$ eV which is again smaller than the value extracted from the resistivity measurement ($E_a=0.106$ eV). In this case, the statistical contribution from the small polarons would be $S=180.9 \mu V/K$. Below 160K, the behavior of the thermopower is characteristic of phonon drag due to dominant electron-phonon scattering [40], and below 75K, the mobile charge carriers are frozen out. Despite the general behavior of this compound which is characteristic of a semiconductor, the value of the Seebeck coefficient is surprisingly smaller than $k_B/e = 87\mu V/K$, below which samples are considered to be metallic.
For $x=0.30$, we notice a large decrease of the Seebeck coefficient, which becomes smaller with decreasing temperature. It was not possible to collect data below 140K, due to the resistance being too high.

The metallic samples present an unconventional behavior that has been previously observed in the case of strongly correlated materials [40]. It comes from the fact that the thermal variation of the thermopower is strongly affected by factors such as electron-phonon scattering and electron-electron correlation and localization. Below $\approx 140K$, the thermopower decreases to 40K (almost reaching the value it had at 300K) then increases again. We cannot associate it with a simple metallic behavior:

$$S = \frac{k_B}{e} \cdot \frac{k_B T}{E_F}$$

(4.7)

and several competing physical mechanisms seem to be present at the same time. Similar phenomenon is found in the case of the Sm- and Pr-based samples as will be presented in the following paragraphs.

c. Specific heat

The temperature dependence of the specific heat $C(T)$ for $Y_{1-x}Ca_xVO_3$ is presented in Figure 4.18. There is a downturn in the $C/T$ curve for the lowest temperatures, which has also been observed in literature [19]. We chose to perform the linear fit of $C(T)/T$ vs $T^2$ above the onset of the downturn. From the fit we extract the value of the electronic term $\gamma$ for each composition. The deviation at low temperatures can be ascribed to low energy excitations including impurities and/or crystal field excitations. We find that $\gamma$ increases with increasing calcium concentration. We extract the effective mass of the conduction electrons from the experimental value of the electronic term as follows:

$$m^* = \frac{m_{th}}{m_{free-el}} = \frac{\gamma_{observed}}{\gamma_{free-el}}$$

(4.8)

It should be mentioned that we derived our $\gamma_{free-el}$ value from the nominal value of the number of conduction electrons in each sample [42]. We plot the value of the effective mass ratio ($m^*$) in Figure 4.19, where one can see that $m^* \approx 25$ for all compositions. Note that for a Mott-Hubbard transition the effective mass should diverge at the insulator-metal transition. We do not observe this phenomenon here.
d. Hall Resistance

The Hall resistance has been measured in the Y-series using the first technique described in Chapter 2. It is possible to extract quite precisely the value of the Hall resistance at a temperature of 115K as can be seen in Figure 4.20. At other temperatures the impedance of the sample can be too small for the samples with high calcium concentration or too large for those with small calcium concentration, which compromises the resolution or the magnitude of the signal. Likewise, we were unable to measure the Hall resistance for the compound with $x=0.10$. The number of charge carriers per formula unit clearly vanishes with decreasing doping concentration. This behavior is often observed instead of the effective mass divergence in the case of a transition from an antiferromagnetic metal to an antiferromagnetic insulator [48].

4.2.3.2 Transport properties of $\text{Sm}_{1-x}\text{Ca}_x\text{VO}_3$

a. Resistivity

The resistivity measurements performed on the $\text{Sm}_{1-x}\text{Ca}_x\text{VO}_3$ compounds are presented in Figure 4.21. The fitted parameters are shown in Table 4.3. For $x \leq 0.20$, the resistivity follows a thermally activated behavior (Equation 4.1). The samples do not present evidence for a variable range hopping mechanism. We notice that the measurable temperature range of the data is smaller than in the Y-based compounds at similar calcium concentrations. The temperature range is essentially the same for both $x=0.10$ and $x=0.20$. 

Figure 4.18: Evolution of the low-temperature specific heat of $\text{Y}_{1-x}\text{Ca}_x\text{VO}_3$.

Figure 4.19: Evolution of the electron effective mass $m^*$ with increasing calcium doping in $\text{Y}_{1-x}\text{Ca}_x\text{VO}_3$. 

104 Chapter 4. Insulator-to-Metal transition in (R,Ca)VO$_3$
There is a large decrease of the activation energy between SmVO$_3$ ($E_a=0.232$ eV) and Sm$_{0.9}$Ca$_{0.1}$VO$_3$ ($E_a=0.088$ eV). The activation energy decreases to 0.054 eV for $x=0.20$.

The type of conduction changes from $x=0.30$: the resistivity decreases with decreasing temperature (Equation 4.4), with an upturn at low temperatures, as is the case for the Y-series. For $x=0.30$, only the electron-electron interactions are present above 130K. Below 60K, the conductivity exclusively follows a $\sqrt{T}$ behavior, with: $\sigma = 78.5 + 21.43 \sqrt{T}$.

In the case of $x=0.4$, the resistivity provides evidence for the presence of electron-phonon scattering and electron-electron interactions above 35K. Only the electron-electron interactions seem to be present in the lower temperature region. An upturn is observed below 15K, although two data points are not enough to fit the conductivity with a $\sqrt{T}$ behavior. The electron-electron interaction yields a $T^2$-dependence down to 15K. The deviation from the calculated temperature dependence of the resistivity at 5K in both $x=0.3$ and $x=0.4$ will be discussed in the Chapter 5.

For $x=0.5$, the whole temperature range can be fitted using electron-electron and electron-phonon interactions.

\textit{b. Seebeck effect}

The data collected from the Seebeck measurements are presented in Figure 4.22, and one can observe two distinct behaviors. In the upper graph, high values of the Seebeck coefficient are measured for $x=0.10$. Using Equation 4.5, one obtains an $E_a$ of 0.01 eV (although this is 8 times lower than the value obtained
from the resistivity measurement, the difference between the two values is smaller than that obtained in the Y-series). The difference between the values obtained from thermopower and resistivity suggests that a small-polaron contribution is again present [40]. Moreover, the mobile carriers become frozen out below 55K.

For $x=0.20$, the values of the Seebeck coefficient have already decreased below $87\mu V/K$ which shows that the sample has an increased number of charge carriers. The Seebeck coefficient is still much larger than in compounds of higher calcium concentration. A value of $E_a=0.00272$ eV is found in the very high temperature range, which is half of the calculated value from the resistivity measurement. Below 200K, the value of the Seebeck coefficient decreases but never follows a metallic behavior and even becomes negative below 50K. It reaches a minimum around 45K, then increases slightly again and becomes positive below 25K.

The compositions that exhibit metallic behavior all present extremely similar values of the Seebeck coefficient. At low temperature, a negative minimum is seen and at approximately 180K, a broad large maximum that may be caused by phonon drag is present. This behavior is similar to that found in $La_{1-x}Ca_xVO_3$ in the metallic region, and also to that in $Y_{1-x}Ca_xVO_3$, but with a different offset. The Seebeck coefficient remains positive over the entire temperature range for $x=0.5$. We cannot properly extract a value of the Fermi energy for the conducting samples. However, the high temperature linear term becomes smaller.
Table 4.3: Fitting parameters for the temperature dependence of the resistivity in Sm$_{1-x}$Ca$_x$VO$_3$. $E_a$ and $\rho_{01}$ are the activation energy and the prefactor in the thermally activated behavior function, respectively; $\rho_{03}$, $a_{e-ph}$ and $a_{e-e}$ are the residual resistivity, the electron-phonon scattering and the electron-electron interactions, respectively.

<table>
<thead>
<tr>
<th>x</th>
<th>$E_a$ (eV)</th>
<th>$\rho_{01}$ (Ω.cm)</th>
<th>$\rho_{03}$ (Ω.cm)</th>
<th>$a_{e-ph}$ (Ω.cm.K$^{-1}$)</th>
<th>$a_{e-e}$ (Ω.cm.K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.232</td>
<td>0.0607</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.088</td>
<td>0.0298</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.054</td>
<td>0.00236</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3 (T≥135K)</td>
<td></td>
<td>0.0033</td>
<td>0</td>
<td>4.1E-8</td>
<td></td>
</tr>
<tr>
<td>0.4 (T≥40K)</td>
<td></td>
<td>0.00054</td>
<td>6.46E-6</td>
<td>2.84E-8</td>
<td></td>
</tr>
<tr>
<td>0.4 (T≤35K)</td>
<td></td>
<td>0.00076</td>
<td>0</td>
<td>5.96E-8</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>0.00029</td>
<td>7.09E-7</td>
<td>5.07E-9</td>
<td></td>
</tr>
</tbody>
</table>

c. Specific heat

The temperature dependence of the specific heat for Sm$_{1-x}$Ca$_x$VO$_3$ is presented in Figure 4.23. A Schottky-like anomaly is apparent in the C/T curve for the lowest temperatures, which probably originates from the crystal field splitting of the Sm$^{3+}$. Schottky anomalies are commonly observed in Sm-related compounds [49]. The amplitude of the anomaly decreases with increasing calcium concentration. We thus performed the linear fit above this anomaly and extracted the values of the electronic contribution to the specific heat. Following the same formula used in the case of Y$_{1-x}$Ca$_x$VO$_3$ (Equation 4.8), we extracted the effective mass for each calcium concentration and the values are plotted in Figure 4.24. Again it corresponds to strong electron-electron interactions resulting in a large effective mass. The effective mass does not diverge on going toward the insulating side of the series. Still, there is a considerable decrease of the effective mass between x=0.2 and x=0.3. At low temperature, the specific heat can be fitted using:

$$C(T) = nR \left( \frac{\Delta}{T} \right)^2 \frac{exp(\Delta/T)}{[1 + exp(\Delta/T)]^2} + \gamma T + \beta T^3$$

(4.9)

The first part of the equation is the Schottky contribution to the specific heat, corresponding to a two-level Schottky function, with n the fraction of magnetic Sm, R the universal gas constant, and $\Delta$ the Kramers doublet splitting. We find that $\Delta$ decreases only very slightly with increasing calcium concentration, whereas
Figure 4.23: Evolution of the low-temperature specific heat of Sm$_{1-x}$Ca$_x$VO$_3$.

Figure 4.24: Evolution of $m^*$ with increasing calcium doping in Sm$_{1-x}$Ca$_x$VO$_3$.

$n$ decreases a lot. Sm is commonly found in a mixed valence state [49–52] as will be discussed in Chapter 5, and we thus believe that we not only have magnetic Sm$^{3+}$ but also non-magnetic Sm$^{2+}$ in the compound. For the undoped sample, we find a fraction of Sm$^{3+}$ within the error bars of the expected value ($n=1$). It thus seems that chemical pressure applied by the introduction of divalent calcium, induces the creation of Sm$^{2+}$. This phenomenon would lead to the creation of more V$^{4+}$ in the compound than if only Sm$^{3+}$ were present. This may lead to a MIT at lower calcium concentration than if only Sm$^{3+}$ ions were present. No other report on the MIT in Sm$_{1-x}$Ca$_x$VO$_3$ being available, it is difficult to make a firm conclusion firmly on this point. However, the presence of Sm$^{2+}$ ions, which are non magnetic ($4f^6$, $J=0$), explains the large difference between the calculated and experimental paramagnetic effective moments in this compound as can be seen in Table 4.4.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Sm$^{3+}$ (%)</th>
<th>$p_{eff}[\text{Sm}]$</th>
<th>$p_{eff}[\text{V}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>80</td>
<td>0.67</td>
<td>2.81</td>
</tr>
<tr>
<td>0.2</td>
<td>73</td>
<td>0.61</td>
<td>2.12</td>
</tr>
<tr>
<td>0.3</td>
<td>51</td>
<td>0.43</td>
<td>1.67</td>
</tr>
<tr>
<td>0.4</td>
<td>48</td>
<td>0.40</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Table 4.4: Fraction of Sm$^{3+}$ ions and corresponding values of $p_{eff}$ for Sm and V spins for each composition.

d. Hall Resistance
The Hall resistance was measured with the second technique described in Chapter 2 and the data are presented in Figure 4.25. The number of charge carriers per formula unit was extracted for all compositions (Fig. 4.26). The value increases rapidly with increasing calcium concentration as the sample goes toward being a metal, in agreement with the other transport experiments.

**Figure 4.25:**
Hall resistance in Sm$_{1-x}$Ca$_x$VO$_3$ (logarithmic scale).

**Figure 4.26:**
Number of charge carriers in Sm$_{1-x}$Ca$_x$VO$_3$ (logarithmic scale).

### 4.2.3.3 Transport properties of Pr$_{1-x}$Ca$_x$VO$_3$

#### a. Resistivity

The resistivity measurements performed on the Pr$_{1-x}$Ca$_x$VO$_3$ samples (Fig. 4.27) show a thermally activated behavior for PrVO$_3$ and Pr$_{0.95}$Ca$_{0.05}$VO$_3$.

For 0.10 $\leq x \leq$ 0.20, a thermally activated behavior (Equation 4.1) is observed at high temperatures and a variable range hopping behavior (Equation 4.2) is observed at lower temperatures, both contributing to the conduction, as reported in Table 4.5. This behavior was also observed in the Y-series. Following Equation 4.3, we can extract from $T_0$ the values of $N(E_F)$, and we obtain $5.07 \times 10^{18}$, $1.84 \times 10^{19}$ and $9.55 \times 10^{19}$ cm$^{-3}$eV$^{-1}$ for $x=0.1$, 0.15 and 0.20 respectively, which shows again how the density of localized states at the Fermi level increases exponentially over this concentration range.

For $x>0.25$, the resistivity decreases with increasing temperature, as expected for Fermi liquid behavior. The data shows an upturn at low temperatures as was observed in the other Ca-doped vanadate series (Paragraphs 4.2.3.1 and 4.2.3.2). For $x=0.25$, below 25K, the conductivity varies $2.87 + 11.49 \sqrt{T}$. Above 125K, the resistivity follows a metallic behavior, with electron-electron interactions leading to a $T^2$ dependence.
For $x=0.3$, the conductivity varies as $4.83 + 11.43\sqrt{T}$ below $15K$, and the resistivity shows the same behavior as the $x=0.25$ compound over the rest of the temperature range. For $x=0.4$, the conductivity varies as $265 + 2.62\sqrt{T}$ below $20K$, but follows a metallic behavior above. For $x=0.5$, an unconventional downturn is observed below $30K$, reminiscent of the formation of a coherent state that is often observed for strongly correlated metals. The resistivity exhibits a combination of electron-phonon scattering and electron-electron interactions although at high temperatures the electron-phonon scattering does not contribute significantly. For $x=0.6$, the conductivity varies as $276 + 2.09\sqrt{T}$ below $15K$ and exclusively shows metallic behavior above. The fitting parameters for the
4.2. Experimental results

Table 4.6: Fitting parameters for the temperature dependence of the resistivity in Pr$_{1-x}$Ca$_x$VO$_3$: $\rho_{03}$, $a_{e-\text{ph}}$ and $a_{e-e}$ are the residual resistivity, the electron-phonon scattering and the electron-electron interaction coefficients, respectively.

<table>
<thead>
<tr>
<th>x</th>
<th>$\rho_{03}$ ($\Omega \cdot \text{cm}$)</th>
<th>$a_{e-\text{ph}}$ ($\Omega \cdot \text{cm} \cdot \text{K}^{-1}$)</th>
<th>$a_{e-e}$ ($\Omega \cdot \text{cm} \cdot \text{K}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 (T$\geq$130K)</td>
<td>0.0037</td>
<td>0</td>
<td>4.28E-8</td>
</tr>
<tr>
<td>0.30 (T$\geq$170K)</td>
<td>0.0037E-5</td>
<td>0</td>
<td>3.019E-8</td>
</tr>
<tr>
<td>0.40 (T$\geq$80K)</td>
<td>0.0035</td>
<td>0</td>
<td>2.004E-8</td>
</tr>
<tr>
<td>0.40 (15K$\leq$T$\leq$75K)</td>
<td>0.0036</td>
<td>0</td>
<td>8.19E-9</td>
</tr>
<tr>
<td>0.50 (T$\geq$55K)</td>
<td>0.0034</td>
<td>3.66E-6</td>
<td>1.239E-8</td>
</tr>
<tr>
<td>0.50 (T$\geq$145K)</td>
<td>0.0038</td>
<td>0</td>
<td>2.06E-8</td>
</tr>
<tr>
<td>0.50 (50K$\leq$T$\leq$145K)</td>
<td>0.0035</td>
<td>0</td>
<td>3.08E-8</td>
</tr>
<tr>
<td>0.60 (T$\geq$50K)</td>
<td>0.0035</td>
<td>0</td>
<td>1.81E-8</td>
</tr>
</tbody>
</table>

compositions from x=0.25 to x=0.60 are reported in Table 4.6.

b. Seebeck effect

The Seebeck measurements are plotted in Figure 4.28. Four distinct behaviors are observed.

The first observed behavior is for high values of the Seebeck coefficient, corresponding to PrVO$_3$ and Pr$_{0.95}$Ca$_{0.05}$VO$_3$. In PrVO$_3$, the Seebeck coefficient could only be measured over a narrow range of temperatures, down to 235K, similar to the resistivity. Below, the mobile charge carriers are frozen out. We extract $E_a$=0.0301 eV. In the case of Pr$_{0.95}$Ca$_{0.05}$VO$_3$, we could extract an activation energy from the range 160K to 300K of $E_a$=0.015 eV, which is similar to the value calculated from the resistivity data.

The second region is in doping the range 0.1$\leq$x$\leq$0.15. The values of the Seebeck coefficient are now more than three times smaller, but the temperature dependence still corresponds to semi-conducting behavior. The measurable range increases, as it does for the resistivity, and one can observe that the mobile charge carriers freeze out below 50K. One can extract $E_a$=0.00285 eV for x=0.10 and 0.0011 eV for x=0.15.

The third region corresponds to 0.2$\leq$x$\leq$0.3. The Seebeck coefficient can be measured down to the lowest temperatures. The thermopower decreases with decreasing temperature and at low temperatures all three compositions reach a negative minimum as observed for Sm$_{0.8}$Ca$_{0.2}$VO$_3$. It is not possible to extract
the Fermi energy for these three compositions but one can clearly notice how the high temperature linear term decreases (especially between $x=0.20$ and $x=0.25$).

The last characteristic region features the high-doping compositions with a behavior similar to that found in $\text{La}_{1-x}\text{Ca}_x\text{VO}_3$ and also for the highest doping of $\text{Y}_{1-x}\text{Ca}_x\text{VO}_3$ and $\text{Sm}_{1-x}\text{Ca}_x\text{VO}_3$. Here a broad maximum is apparent at high temperature. It is interesting to note that for $x=0.4$ and $x=0.5$, the thermopower remains positive over the entire range of temperatures, while it reaches negative values for $x=0.60$ (between 40K and 125K). It seems that the sign and value of the Seebeck coefficient becomes independent of the calcium concentration above a certain doping level.

c. Hall Resistance

The Hall resistance was measured with the second technique described in Chapter 2 and the data are presented in Figure 4.29. The extracted number of charge carriers per formula unit are shown in Figure 4.30. The value increases rapidly with increasing calcium concentration as the sample goes toward the metallic state, the largest increase being found in the range $0.15 \leq x \leq 0.25$.

4.3 Summary

It is useful to summarize the experimental results in order to analyze the nature of the MIT in these compounds. From the experimental results we can clearly distinguish three doping regimes for each of the calcium-doped rare-earth vanadates:
4.3.1 AFM insulator region

For low calcium doping, the compounds are still magnetically ordered, and the experimental effective magnetic moments are close to the theoretically expected values. The resistivity of the samples exhibits two types of behavior in the insulating region. Firstly, Sm$_{1-x}$Ca$_x$VO$_3$ exhibits thermally activated behavior over the entire temperature range (Table 4.3). Secondly, Y$_{1-x}$Ca$_x$VO$_3$ and Pr$_{1-x}$Ca$_x$VO$_3$ display thermally activated behavior for low doping concentration; but as the calcium concentration increases, the low-temperature resistivity follows the variable range hopping behavior, as often observed in the case of an Anderson transition. This happens at $x_1 > 0.1$ and 0.05 for Y$_{1-x}$Ca$_x$VO$_3$ and Pr$_{1-x}$Ca$_x$VO$_3$, respectively.

Evidence for the insulating state is given by the number of charge carriers, which is extremely low for these compositions, as well as the thermopower which yields a Seebeck coefficient following the expected semi-conducting behavior. The activation energies (reported in Tables 4.1, 4.3 and 4.5) show a large decrease between the undoped parent compound and the first doped composition. Moreover, the activation energy decreases towards zero with increasing calcium concentration as the MIT is approached (Fig. 4.31). Concerning the exact value of the calcium concentration at the transition, more compositions would need to be measured in order to determine accurately the critical composition. We find evidence in the thermopower experiment that the critical compositions should be close to the point where the Seebeck coefficient decreases and the temperature...
dependence changes radically.

4.3.2 AFM metal region

As the calcium concentration increases further, all transport measurements show metallic behavior, as evidenced by the changes in the transport properties at the border of the AFM insulator region. The resistivity shows, for some compositions, an anomalous low temperature behavior that will be discussed in detail in the next Section. One would expect the magnetic properties to exhibit Pauli paramagnetic behavior over the entire range of temperature. This is not true for these compounds, which first become antiferromagnetic metals. Concerning the crystal structure, it is difficult to conclude that the small anomalies observed in the structural parameters are linked to the insulator to metal transition. Only the transport properties unambiguously confirm this fact.

4.3.3 PM metal region

The region where the compounds are AFM metals is quite broad, and only for high concentrations of calcium do the samples provide no evidence of magnetic ordering. This occurs, for example, at $x=0.5$ in $\text{Sm}_{1-x}\text{Ca}_x\text{VO}_3$, and $x=0.6$ in $\text{Pr}_{1-x}\text{Ca}_x\text{VO}_3$. However, there is no change in the crystal structure or electronic properties here.

4.4 Discussion

As mentioned in the summary, the MIT follows a slightly different pattern in the case of $\text{Sm}_{1-x}\text{Ca}_x\text{VO}_3$. We will discuss the two types of transitions based on the different experimental techniques.

4.4.1 Structural properties

The diffraction experiments show that all of the studied compositions are stable in the orthorhombic perovskite structure. It was not possible to locate the MIT by only considering RT structural data. However, once the MIT had been defined by other techniques, we could confirm that the structural anomaly observed in each series coincides with the transition. We also note that the volume anomaly becomes more pronounced with increasing rare-earth radius.
4.4. Discussion

4.4.1.1 Large volume decrease

It may be expected that the volume increases with increasing calcium concentration, as $r_{Ca^{2+}} > r_{R^{3+}}$. However, we observe a decrease of the unit-cell volume for each series (Fig. 4.1). Part of the decrease is due to the metallic character of the compounds with high calcium concentration. If we consider the ionic sizes we notice: $r_{V^{3+}} > r_{V^{4+}}$ and $r_{Y^{3+}} < r_{Sm^{3+}} < r_{Pr^{3+}} < r_{La^{3+}} < r_{Ca^{2+}}$. We observe that the larger the R-site ionic radius, the larger the decrease in volume between RVO$_3$ and CaVO$_3$. We report the relative changes in size of the A-site atom and of the volume in Table 4.7. It is clear that even when the relative size-change on the A-site is large (as in the case of the Y-series), the volume still decreases. The relative size change on the B-site going from $V^{3+}$ to $V^{4+}$ is -9.38%.

If we consider the V-O bond distances, we can compare the distances observed for an insulator with octahedral $V^{3+}$ (our RVO$_3$, R= rare-earth or yttrium), with those present in an insulator with octahedral $V^{4+}$. For this purpose we use the compound Sr$_2$VO$_4$ [53, 54]. It is a layered Ruddlesden-Popper n=1 structure, with layers of corner-shared octahedra separated by SrO layers and serves as a useful comparison. The 4 V-O bond lengths in the corner-shared ab plane are 1.917Å, and the 2 V-O to the apical oxygens are 1.986Å, giving an average V-O of 1.940Å. In these Ruddlesden-Popper structures the distances to the apical oxygens are often elongated. It is thus likely that in an insulating $V^{4+}$ perovskite the average V-O distance would be less than 1.940Å. This should be compared to the average value of 1.915Å in metallic CaVO$_3$ and 1.921Å in metallic SrVO$_3$, which shows a large reduction from the average V-O bond distance of 2.00Å in insulating RVO$_3$. In conclusion, it seems that the presence of $V^{4+}$ has a large effect on shrinking the octahedra. However, it is difficult to analyze quantitatively whether the shrinking of the octahedra or the metallicity is the main factor responsible for the large decrease of the unit-cell volume.

<table>
<thead>
<tr>
<th>R-site atom</th>
<th>R-site size change (%)</th>
<th>Volume change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>+13.50</td>
<td>-4.50</td>
</tr>
<tr>
<td>Sm</td>
<td>+8.06</td>
<td>-7.76</td>
</tr>
<tr>
<td>Pr</td>
<td>+3.08</td>
<td>-9.70</td>
</tr>
<tr>
<td>La</td>
<td>-1.47</td>
<td>-11.6</td>
</tr>
</tbody>
</table>

*Table 4.7:* Relative changes in volume and in size of the R-site cation between RVO$_3$ (R=Y, Sm, Pr, La) and CaVO$_3$

115
4.4.1.2 Structural anomaly at the onset of the transition

We do not observe a clear structural change at the onset of the MIT. Végard’s law predicts a linear variation of the unit-cell parameters with doping in a solid solution. However, in the presence of an insulator-metal transition, the virial theorem of classical mechanics should be considered:

\[ 2\langle K \rangle + \langle V \rangle = 0. \]

When passing from a localized to itinerant electronic state the mean kinetic energy of the electron of the VO$_3$ array should decrease discontinuously. This would be compensated by a discontinuous change in the mean potential energy and hence in the V-O bondlength, resulting in a discontinuous volume change and a first-order transition. However, even if such strong electron-lattice interactions are expected, powder diffraction at room temperature may not be able to reflect the changes in the structure for this kind of transition. We clearly observe a deviation from Végard’s law in the Y-, Sm- and Pr-series. It is most pronounced in the case of Pr$_{1-x}$Ca$_x$VO$_3$ and gradually decreases in magnitude with decreasing ionic radius of the rare-earth (or yttrium). By comparison, La$_{1-x}$Ca$_x$VO$_3$ shows a clear first-order discontinuity at the onset of the MIT [40].

In conclusion, we observe that the MIT causes a structural transition that is more pronounced for large tolerance factors. The tolerance factor (and ionic radii of the R- and M-site cations) is not only responsible for the stability of the orthorhombic perovskite structure, but also determines structural changes induced by a MIT (and vice versa). Indeed, the tolerance factor determines the bandwidth, thus as the bandwidth decreases, the amount of kinetic energy will increase, so the magnitude of the volume discontinuity will decrease.

4.4.2 Magnetic properties

Before discussing the behavior of the magnetic properties across the MIT, we will mention the high temperature behavior in the Y-series. It should be noted that the effective moment of the parent compound (YVO$_3$) was extracted without a temperature-independent paramagnetic (TIP) term in a previous report [39]. When plotting the inverse susceptibility vs temperature, the authors observed two distinctly different slopes below and above 200K. This temperature corresponds in YVO$_3$ to the OO. Therefore, the authors fitted the data with different Curie-Weiss curves below and above 200K with Curie-Weiss behavior. We argue that this behavior is unrelated to OO. We observe that the change in slope is present over the entire range of compositions (Figs. 4.33 and 4.34) including compositions for which the OO is not present any more [3]). Moreover, the effective moments based on Curie-Weiss behavior only are not realistic. However, adding a TIP
term to the susceptibility results in us and other authors \[24, 25\] obtaining the expected values of $p_{\text{eff}}$ and a good fit over the entire temperature range.

Figure 4.33:
Inverse susceptibility of $Y_{0.7}\text{Ca}_{0.3}\text{VO}_3$ showing apparent anomaly at $T=200\text{K}$ which can be accurately fitted with Curie-Weiss behavior when including a TIP.

When the parent compounds $\text{YVO}_3$, $\text{SmVO}_3$ and $\text{PrVO}_3$ are doped with $\text{Ca}^{2+}$ on the rare-earth site, it leads to a stronger superexchange due to increasing V-O-V angles. As the dopant concentration increases, it eventually results in an itinerant state that is Pauli paramagnetic. In the case of these three compounds we observe a transition from an antiferromagnetic insulator to an antiferromagnetic metal. There is a large decrease of $p_{\text{eff}}$ when the compounds become metallic, but this is not an accurate method of determining the concentration at which the transition takes place. This type of transition (AFM-I to AFM-M) has been observed in other vanadates (e.g. $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ \[2\]) and is explained \[48\] by the folding of the Brillouin zone due to the superstructure of the magnetic periodicity which creates a completely filled lower band. Carriers are doped into small pockets of the Fermi surface whose Fermi volume vanishes at the transition.

The octahedral tilting (Fig. 4.4) decreases with increasing calcium concentration. The decrease in tilting strengthens the superexchange and should lead to an increase of $T_N$. However, the increase in $V^{4+}$ and metallicity tend to destroy the long range antiferromagnetic order and decrease $T_N$. As a result, the decreasing V-moment, compensated by a decrease in octahedral tilting, results in a small decrease of $T_N$.

We observe that the decrease of $T_N$ is larger for the Pr-series than for the
Sm-series, and more pronounced for the Sm-series than for the Y-series. This can be related to the tolerance factor value, as explained in the discussion of the structural properties. However, one should be careful in the analysis of the magnetic properties: we have already observed that there are many different reports of Néel temperature variations with doping. We conclude that there does not seem to be a strong correlation between the MIT and the magnetic properties.

4.4.3 Transport properties

The electronic transport properties seem to be the most precise tool to describe the MIT in these calcium doped vanadates. As summarized above, we find similar behavior for the Y- and Pr-series, and a slightly different behavior for the Sm-series.

4.4.3.1 Y-Pr-series

$x < x_1$: The compounds display thermally activated behavior both in the resistivity and thermopower data. However, it should be noted that the formation of small polarons leads to a lower value of the activation energy in the thermopower experiments than in the resistivity experiments. For these compositions, the number of charge carriers is small and at low temperatures the resistance is too large to measure. These features can be described using a model where the two Hubbard bands are separated by an energy $U$. The activation energy corresponds to the thermal excitation from the lower Hubbard band to the upper band.

$x_1 < x < x_c$: As the calcium concentration increases, the mechanism of variable range hopping appears at low temperatures and dominates the thermally activated behavior. This is evident from the thermopower experiments, signaled by a change in sign of the temperature dependence of the Seebeck coefficient. It corresponds to a filling of states in the Hubbard gap, and the band tails start to overlap. However, metallic behavior is not yet observed, as explained by Anderson and Mott [55]. Disorder leads to the localization of electrons (Anderson localization). This phenomena is evidenced by a power-law temperature dependence of the resistivity described by variable range hopping.

$x > x_c$: For higher calcium concentration, the compounds are metallic, the number of charge carriers has increased markedly, and the transport behavior can be described by Fermi-liquid theory [48]. However, the resistivity at low temperature exhibits a $\sqrt{T}$ dependence. This is observed for both series. In the case of the Y-series, it disappears for higher calcium concentrations, but not
for the Pr-series. Fermi Liquid theory assumes a system to be homogeneous. However, if it contains defects that scatter the electrons, they can back-scatter instead of moving freely. This leads to anomalous low-temperature behavior in such disordered metals.

Concerning the localization effects, it has been observed that if a metal contains a high enough concentration of defects, electrons will be weakly localized. It will then go from a delocalized to localized state with decreasing temperature signaling Anderson localization. This theory predicts that in a 3D system the conductivity will follow a $\sqrt{T}$ dependence. It has been shown that an external magnetic field will suppress this localization, as it destroys the probability of a particle returning to a given point. This will lead to a decrease in the resistivity, known as negative magneto-resistance. We do not observe such behavior here.

The low-temperature behavior of the resistivity is also the result of other interactions. It has been shown that in a disordered Fermi liquid, anomalous behavior occurs close to the Fermi level, because of the diffusive character of the electron motion. This leads to a $\sqrt{T}$ dependence of the resistivity at low temperatures. However, in this case one expects a positive magnetoresistance.

It is possible that the anomalous low temperature behavior originates from both weak-localization and electron interaction effects. However, experimentally, weak localization is mainly responsible for the anomalous behavior in the Y- and Pr-series.

Kadowaki and Woods found phenomenologically that the electronic specific heat coefficient scales linearly with the coefficient of the $T^2$ of the resistivity for compounds in which the electron-electron interactions dominate [56]. For $Y_{1-x}Ca_xVO_3$ we find a value that is in good agreement with this 'universal' behavior. This is evidence that the $T^2$ dependence of the resistivity originates from electron-electron interactions as described by Fermi-liquid theory.

In conclusion, we find that the Y- and Pr-series exhibit weak localization effects, known as Anderson localization. The localization is induced by disorder and leads to an intermediate state where variable range hopping is observed.

### 4.4.3.2 Sm-series

The MIT observed in $Sm_{1-x}Ca_xVO_3$ is more straightforward than in the other series. For low calcium concentrations, the compounds display thermally activated behavior as expected for semiconducting samples. The activation energy from the resistivity is larger than that obtained from the thermopower, which we associate with small polaron formation. The activation energy decreases with increasing
calcium concentration (Fig. 4.31). This phenomenon has been is explained above.

As the calcium concentration increases, the Hubbard bands overlap which leads to metallic behavior, as observed experimentally. In this case disorder does not lead to localization. However, we still observe anomalous low-temperature behavior in the resistivity, which we believe is here dominated by electron interactions leading to a $\sqrt{T}$ dependence at low temperatures. The positive magnetoresistance that was observed will be discussed in the next chapter. It has different origin. One more feature occurs in the metallic regime: the relationship noticed by Kadowaki and Woods applies well to these compounds [56]. This confirms the role of the electron-electron correlations resulting in a $T^2$ dependence of the resistivity. Once more we should note that the presence of Sm$^{2+}$ ions as revealed by specific heat experiments leads to a higher concentration of V$^{4+}$. Therefore, the transition might appear at a higher calcium concentration if only Sm$^{3+}$ were present. In conclusion, the transport properties indicate that Sm$_{1-x}$Ca$_x$VO$_3$ goes through a Mott-Hubbard MIT.

4.5 Conclusion

The more distorted the orthorhombic perovskite structure, the more difficult it is to observe the MIT in the crystal structure, at least at room temperature with a lab diffractometer. The magnetic properties alone are also unable to determine the position of the MIT with respect to doping even if a transition from antiferromagnetic to Pauli-paramagnetic behavior is observed. We have deduced the nature of the insulator to metal transition from the electron transport measurements. Although Sm$_{1-x}$Ca$_x$VO$_3$ exhibits only a Mott-Hubbard transition,
$Y_{1-x}Ca_xVO_3$ and $Pr_{1-x}Ca_xVO_3$ also show Anderson localization. Here, disorder leads to an intermediate state before the metallic state. We present a sketch of the phase diagram of the calcium-doped vanadates in Figure 4.35.
Appendix A  Lattice parameters

Figure Apx. A.1: Unit-cell parameters of $R_{1-x}Ca_xVO_3$, with $R$=Y (a), Sm(b) and Pr (c)
References

References


[49] I. M. Sutjahja; *Crystal Growth and Physical Properties of T*-phase SmLa$_{1-x}$Sr$_x$CuO$_4$ and T-phase La$_{1.6}$Nd$_{0.4}$Sr$_x$CuO$_4$*; Ph.D. thesis; University of Amsterdam (2003)


