CHAPTER 5

Positive Magnetoresistance in (Sm,Ca)VO\(_3\)

5.1 Introduction

As mentioned in Chapter 1, magnetoresistance (MR) signals the change of the electrical transport properties in response to applied magnetic fields. MR is a well studied subject in the transport properties of solids. The origin is as varied as the large number of scattering phenomena that occur in pure metals and semiconductors and at impurities, defects and interfaces. In general, the Pauli principle in metals and semiconductors results in large kinetic energies of the conduction electrons. Therefore, the Zeeman energy from applied magnetic fields is usually a small perturbation. Consequently, MR is conventionally small and, at most, of the order of a few percent. Furthermore, applied magnetic fields align the electron spin of the conduction electrons, which generally leads to an enhancement of the conductivity and decreased scattering. MR therefore usually has negative values in magnetic compounds. The MR of (Sm,Ca)VO\(_3\) is remarkable because it is large and positive. We have observed in the previous chapter that the transport phenomena of (Sm,Ca)VO\(_3\) are associated with the emergence of a strongly correlated metal and weak localization phenomena at low temperature, and in this chapter, we will discuss the MR found in this series.

Perovskite-type manganites are well-known to exhibit negative colossal magnetoresistance (CMR) associated with a metal-insulator transition (MIT) and
since the magnetic field shifts the temperature of the MIT \([1]\) in these systems the MR is extremely high. Values as high as 1300\% have been reported at room temperature \([2]\). Such effects, when optimized, can be used for magnetic and electric device applications. In recent years large MR effects have thus attracted much attention. In the early 1990’s, negative giant magnetoresistance (GMR) was found in granular alloys consisting of ultrafine Co-rich precipitate particles in a Cu-rich matrix \([3, 4]\). This phenomenon was modeled using spin-dependent scattering at interfaces between the particles and matrix as well as with spin-dependent scattering in the Co-rich particles. GMR had previously only been reported in multilayered structures, arising from the reorientation of single-domain magnetic layers. For example in \((001)\text{Fe}/(001)\text{Cr}\) superlattices, the GMR is ascribed to spin-dependent transmission of the conduction electrons between Fe layers through Cr layers \([5]\). The magnitude of the effect at room temperature, the ability to miniaturize the device structure, the reproducibility and manufacturability have turned such GMR systems into sensors of practical importance. GMR has allowed the continued miniaturization of magnetic storage devices and currently forms the sensor mechanism to probe the magnetic state in hard disk drives, replacing bulkier pick-up loops.

Giant positive magnetoresistance has been observed in metallic \(\text{VO}_x\) thin films \([6]\). The MR was anisotropic, and the authors found that it was strongly dependent on temperature and oxygen content. The positive MR is extremely large (70\%) and was ascribed to the interplay of electron-electron interactions and disorder, although theory predicts a much smaller effect. Alternative hypotheses related to an inhomogeneous magnetic susceptibility and the proximity of the system to a magnetic instability were also proposed by the authors. Positive MR has been observed in stoichiometric \(\text{CaVO}_3\) \([7]\). At low temperatures, this compound shows a positive MR of 14\% in an external magnetic field of 9T and resistivity measurements indicate Fermi-liquid behavior. The changes in resistivity induced by a magnetic field are proportional to \(H^{1.74}\). This positive MR is ascribed to quantum interference effects (QIE) originating from the Coulomb interactions that are enhanced by disorder and that had been previously observed in disordered ferromagnets like \(\text{Fe}_{1-y}\text{Co}_y\text{Si}\) where the same electrons are responsible for the magnetism and electrical conduction \([8]\). More surprisingly, Chen et al. have reported a similar phenomenon in the metallic phase of perovskite-type manganites \([9]\). In these compounds, the \(e_g\) electrons are responsible for the electrical conduction whereas the \(t_{2g}\) electrons form the local spins responsible for the magnetism and act as scattering sites for the conduction electrons. The authors report a positive MR below 50K which is as high as 20\% at 4.2K in 8T, show-
ing how disorder effects and Coulomb interactions are of importance in doped RMnO$_3$.

More generally, MR effects can be associated with electronic (magnetic) phase transitions, reflecting the influence of the magnetic field on the transition temperature and on the electronic states on either side of the transition. In (Sm,Ca)VO$_3$, the large positive MR seems to be associated with a first order transition, and we shall investigate the origin of this transition based on localization effects as well as possible electronic/magnetic ordering leading to such a transition.

## 5.2 Experimental Results

We define the magnetoresistance as:

$$MR(H) = \frac{\rho(H) - \rho(0)}{\rho(0)}$$

We measure a large positive MR of 24% in Sm$_{0.7}$Ca$_{0.3}$VO$_3$ and 20% in Sm$_{0.6}$Ca$_{0.4}$-VO$_3$ below 10K, in fields of several Tesla.

In Chapter 4, we observed that it was not possible to fit the 5K data point in the resistivity curves of Sm$_{0.7}$Ca$_{0.3}$VO$_3$ and Sm$_{0.6}$Ca$_{0.4}$VO$_3$. We can clearly see in Figures 5.1 and 5.2 that the value of the resistance at 5K is much lower than expected when extrapolating the temperature dependence of the resistance. We thus repeated the experiment in a magnetic field of 5T, and observed that although there was no field dependence between 10 and 300K, the value at 5K now corresponds to that expected from the temperature dependence of the resistance. We note that when measured in zero field, the resistance is 24% smaller (20% smaller in Sm$_{0.6}$Ca$_{0.4}$VO$_3$), at 5K.

It became of interest to focus on the low-temperature part of the resistance. One observes a clear discontinuous transition below 8.5K and 7.5K for x=0.3 and 0.4 respectively when the temperature is decreased (Figs. 5.3 and 5.4). When an external magnetic field is applied, the transition shifts toward lower temperatures (Fig. 5.5). We find that the observed transition does not correspond to a transition between two different types of conduction. The transition only induces a lowering of the resistance in the sample.

When the field dependence is measured at fixed temperature (Fig. 5.6) the transition from one state to the other is clearly observed, and the observed positive MR has a maximum of 24%.

We observe for x=0.30 at low fields a negative MR of approximately 3%. This can be ascribed to a more conventional type of MR. At higher fields the positive
MR, arising from a different mechanism, dominates and the total MR is 24%.

A small hysteresis in the MR is observed (Figs. 5.6 and 5.7) on increasing and decreasing the magnetic field, which firstly points out the involvement of the magnetic cations, and secondly indicates that the transition is first-order.

**In summary:** Experimental data reveal that a first order transition involving a large decrease (more than 20%) of the resistance occurs at low temperatures in Sm$_{1-x}$Ca$_x$VO$_3$ ($x=0.3$ and 0.4). This transition shifts toward lower temperature with applied magnetic field. The shift is roughly -1K per Tesla.
5.2. Experimental Results

**Figure 5.3:**
Field dependence of the low-temperature anomaly in the resistance of Sm$_{0.7}$Ca$_{0.3}$VO$_3$.

**Figure 5.4:**
Field dependence of the low-temperature anomaly in the resistance of Sm$_{0.6}$Ca$_{0.4}$VO$_3$.

**Figure 5.5:**
Temperature dependence of the critical field (Hc) for Sm$_{1-x}$Ca$_x$VO$_3$ (x=0.3 and x=0.4).
5.3 Discussion

As discussed in the introduction, MR can result from changes in the intrinsic conduction and scattering mechanisms. It can also arise from conduction between dissimilar materials at interfaces or at phase transitions. We will now discuss the possible origins of the unusual positive MR in Sm\(_{1-x}\)Ca\(_x\)VO\(_3\).

5.3.1 Disorder effects

As was mentioned in Chapter 4, we observe in Sm\(_{1-x}\)Ca\(_x\)VO\(_3\) an increase of the resistivity at low temperatures for \(x=0.3\) and \(x=0.4\). We have shown that it corresponds to a \(\sqrt{T}\) dependence of the conductivity in this temperature range. We shall explain the phenomenon in more detail here.

Weak electronic disorder is ascribed to impurities that scatter Bloch waves. This phenomenon leads in metals to the Boltzmann transport equation for quasiparticles, so that at low temperature the resistivity will have the form

\[ \rho(T) = \rho_0 + AT^n \]

This can be modified in the case of strong disorder by forcing some average periodicity on the system \([10]\). However, this is far from being sufficient and detailed experimental data have shown that many compounds display an anomalous low temperature behavior. The conductivity of compounds with weak disorder is usually a function \(\sqrt{T}\) in 3D systems and this is ascribed to weak localization. One should differentiate the phenomenon of Anderson localization (dealing with the nature of the wave function of a single electron in the presence of a random potential) and interactions between electrons\(^1\).

Elastic scattering of electrons from impurities and lattice defects determines the residual resistance of metals at low temperatures. The scattering by random potentials will cause the Bloch waves to lose coherence on the length scale of the mean free path (the distance over which an electron fluctuates by about 2\(\pi\)). In the case of very weak disorder, the wavelength of the electron is smaller than the mean free path and the wave function remains extended throughout the sample. However, in the case of strong disorder, Anderson showed that the wave function will localize. In this case, Altshuler \textit{et al.} predicted that the \(\sqrt{T}\) dependence of the resistivity at low temperature would be suppressed by (even small) magnetic

\(^1\)Two excellent reviews on disordered electronic systems are available: P.A. Lee and T.V. Ramakrishnan in Reviews of Modern Physics 57, 287 (1985) and A.D. Rata in her PhD thesis 2004.
fields by destructive interference, and leading to a negative MR [11]. The field
dependence of the conductivity follows a $\sqrt{H}$ dependence [10]. It could thus be
possible that the negative MR observed in low magnetic fields for $x=0.3$ may
originate from this electron localization.

It has been shown that electrons do not freely propagate as was at first thought,
but are instead diffusive, which leads to corrections to the Fermi-liquid theory of
metals being necessary. Altshuler and Aronov have shown that interactions (due
to the diffusive character of the electron motion) in a disordered (metallic) system
lead to singularities near the Fermi level which are much stronger than those
observed in the least disordered systems [12, 13] (also predicted by Brinkman and
Engelsberg for spin diffusion [14]). They found an unexpected behavior in the
density of states which corresponds to the anomalous behavior of the transport
properties. Electron interaction effects in the presence of a random potential
indeed lead to a $\sqrt{T}$ dependence of the conductivity, although these effects are
different from the Anderson localization model mentioned above.

The weak localization originating from the interaction effects among electrons
leads to a positive MR. A field dependent term is added to the field independent
temperature dependence of the resistivity. The positive MR can be proportional
to $\sqrt{H}$ (for $g\mu_B H > > k_B T$). If $g\mu_B H < < k_B T$, the MR should be proportional
to $H^2$. However, it has been shown that when taking into account spin-orbit
interactions, the induced MR is in fact even smaller than that due to the Zeeman
effect. In our case, we observe a large MR of over 20%. Moreover, we observe a
discontinuous change of $\rho(T,H)$. 

![Figure 5.6: Magnetoresistance vs magnetic field in Sm$_{0.7}$Ca$_{0.3}$VO$_3$ for fixed temperatures.](image1)

![Figure 5.7: Magnetoresistance vs magnetic field in Sm$_{0.6}$Ca$_{0.4}$VO$_3$ for fixed temperatures.](image2)
5.3.2 Mechanisms leading to a phase transition

When considering the Sm and V ions, one can think of a number of ordering phenomena that would lead to transitions.

5.3.2.1 Schottky anomaly

As mentioned in Chapter 4, the specific heat of Sm$_{1-x}$Ca$_x$VO$_3$, without applying an external magnetic field, reveals a Schottky anomaly due to the crystal field splitting of the Sm 4f electronic energy levels. We present again the anomaly for each composition in Figure 5.8. The Schottky anomaly is commonly found for Sm-related compounds with Sm$^{3+}$ cations. Field dependence measurements of the specific heat have been performed for x=0.30 (Fig. 5.9). Applying external magnetic fields as high as 8T does not lead to a noticeable shift of the Schottky anomaly. This indicates that the Zeeman splitting of the doubly degenerate levels is not involved, but only the crystal field splitting which is, as expected, field independent. We note again that the transition in resistance seems to be first-order and that it shifts with applied fields to lower temperature. We do not observe an anomaly in the specific heat corresponding to this first-order transition. This may be explained by the fact that the entropy of the phenomenon leading to the transition is extremely small when compared to the amplitude of the Schottky anomaly.

5.3.2.2 Charge ordering of vanadium

It is possible to obtain valence state ordering between V$^{3+}$/V$^{4+}$. It has been shown in the manganites (e.g. Nd$_{0.5}$Sr$_{0.5}$MnO$_3$) that a gap in the density of states at E$_F$ is necessary for the charge ordered state to be stable [15]. The opening of the gap leads to a large increase of the resistivity and the transition is first-order. The gap collapses on applying a magnetic field. In our compound, where nearly all of the magnetization originates from V, we do not find an anomaly in the magnetization data that would indicate a spin-state transition associated with a charge ordering temperature. When considering $\rho$(T), we obviously do not observe an increase in the resistivity related to the opening of a gap, but instead a decrease in the resistivity.
5.3.2.3 Spin ordering or reordering

As can be seen in Figure 5.3 (5.4), the transition temperature decreases with magnetic field from \( \approx 8.5 \text{K} \) (7.5K) for \( x=0.3 \) (0.4) with a slope of \( \approx -1\text{K}/\text{T} \). This implies that the transition is most likely caused by a phase transition involving a magnetic ion with \( S \approx 1\mu_B \), because then \( k_BT_c \approx gSH_c \). This could indicate that a reordering of the V spins or an ordering of the Sm spins takes place. Sm experiences the effective field of the vanadium spins and might begin to order below \( T_N \), but full long-range ordering at the transition is still possible. In any case, the antiferromagnetic ordering would then open a gap over part of the Fermi surface which could be suppressed by an applied magnetic field. Therefore, antiferromagnetic ordering typically increases the resistivity at \( T_N \). However this feature is not observed here. We observe a decrease of the resistivity, and it occurs as a first order transition with hysteresis. Moreover, the opening of a gap would not only increase the resistivity, but would also lead to negative MR as the gap decreases with magnetic field.

On the other hand, one can also consider the possibility that the ordering of Sm-spins decreases the scattering of the conduction electrons, which leads to an enhancement of the conductivity. Applying a magnetic field would suppress the ordering of the Sm spins, which would lead to the shift in transition temperature. However, we find no evidence in the magnetization data for ordering of the Sm spins, although this could be due to the fact that the magnetic moment of Sm\(^{3+}\) is
smaller than that of $V^{3+}$ (Table 5.1). Moreover, the $V$ spins are canted which gives rise to a ferromagnetic moment, which may render an antiferromagnetic ordering of $Sm$ spins unobservable. This scenario leaves the magnetic field-independent Schottky anomaly unexplained and another origin to the phenomenon should be considered.

5.3.2.4 Mixed valence state of Sm ions

From the Schottky anomaly induced by the crystal field splitting of the $Sm$ ground state, it is possible to calculate the proportion of magnetic $Sm^{3+}$ present in the compound. In the undoped $SmVO_3$ compound 97 (±3)% of the $Sm$ ions are magnetic $Sm^{3+}$, as expected. The situation is different with increasing doping. As mentioned in Chapter 4, not all of the $Sm$ ions are in the $Sm^{3+}$ valence state with increasing $x$. The proportion of $Sm$ ions in the $3+$ state are listed as a function of $x$ in Table 5.1 (from Equation 4.9). A mixed-valence state of the $Sm$ is present, involving the magnetic $Sm^{3+}$ ($4f^5$, $J=5/2$) and the non-magnetic $Sm^{2+}$ ($4f^6$, $J=0$).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$Sm^{3+}$ (%)</th>
<th>$p_{eff}[Sm]$</th>
<th>$p_{eff}[V]$</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 5.1: Fraction of $Sm^{3+}$ ions and corresponding values of the $p_{eff}$ for $Sm$ and $V$ spins for each composition.

Various studies have shown that several rare-earth ions (in particular $Ce^{3+}/Ce^{4+}$, $Sm^{2+}/Sm^{3+}$, $Yb^{2+}/Yb^{3+}$) have a tendency to present mixed valence states. The most studied of such compounds are chalcogenides and intermediate valence Kondo insulators\(^2\). A mixed valence state of cerium has also been found in $Ce_{1-x}Sr_x VO_3$ [16]. Concerning $Sm$ related compounds, the most well-known is SmS where the valence of the Sm ion gives either a metal ($Sm^{3+}$) or a semi-conductor ($Sm^{2+}$) [17, 18]. More recently, mixed-valent $Sm$ has been found in cuprates through specific heat experiments [19] and in fullerides through diffraction experiments [20, 21]. The valence of the $Sm$ ion (or the value of its

intermediate valence) depends on its coordination in the crystal structure, the applied pressure and the chemical potential.

In Sm$_{2.75}$C$_{60}$, the size of the tetrahedral hole is such that either the slightly larger Sm$^{2+}$ or smaller Sm$^{3+}$ can be accommodated [20]. In this case the transition from an intermediate valence state (2+$\epsilon$) to a lower valence state (2+) is purely temperature induced [20]. Applied external pressure can increase the valence of the Sm ion toward Sm$^{3+}$ [21]. Changing the valence of the rare-earth ion is usually achieved by applying large external pressures [22–24]. However, studying the properties of a compound under high pressure can be difficult, and it has been shown that chemical pressure can efficiently tune the valence state of the rare-earth ion [17, 25, 26]. For example, in SmB$_6$ doping with the larger La$^{3+}$ decreases the valence state of the Sm ion, whereas doping with the smaller Y$^{3+}$ increases the valence state [27]. In the case of Sm$_{1-x}$Ca$_x$VO$_3$ when x=0, the cubic cage formed by the surrounding oxygens may not accommodate the larger Sm$^{2+}$ (at least at ambient pressure), hence the observed valence of the samarium. As the Sm$^{3+}$ is substituted by the larger Ca$^{2+}$, it would become possible for the Sm$^{2+}$ also to fit in the structure (on the same crystallographic site as the Sm$^{3+}$ and Ca$^{2+}$). Therefore, chemical pressure resulting from the bigger calcium cation would induce the mixed valence state of Sm.

We have already mentioned that in samarium fulleride, the valence transition can be purely temperature-induced. In Gd-doped SmS a sufficient amount of Gd induces a change from a mixed valent state to Sm$^{3+}$ at room temperature. However, in a narrow doping range a temperature-induced first-order electronic transition takes place at low temperatures [17]. This changes the valence from Sm$^{3+}$ to a lower mixed-valence state. It has been shown that the temperature dependence of rare-earth valence fluctuations can be extremely different from one system to another [28]. A temperature-induced electronic phase transition changing the valence state of the Sm ion is thus possible in Sm$_{1-x}$Ca$_x$VO$_3$.

A decrease of the valence state of the Sm cations should also lead to lattice changes due to the difference in cationic size. As mentioned in Chapter 4, in (Sm,Ca)VO$_3$ compounds the overall lattice changes are dominated by the increasing metallic character. The changes in the unit-cell volume with doping are not linear, as would be expected from Végard’s law. We instead observe below the MIT an upward deviation from Végard’s law (Apx. A.1b in Chapter 4). Slight upward deviations in the $c/a$ and $b/a$ ratios are also observed in (Sm,Ca)VO$_3$ for $x=0.1$ and $x=0.2$ and not in the other compounds studied in Chapter 4 (Figs. 4.3 and 4.2). For higher concentrations of calcium, the more rapid decrease in the unit-cell parameters with doping is caused by the increasing metallic character of
the compounds, which will most likely obscure any effect due to a valence change in Sm. However, when considering the other compounds studied in Chapter 4, one can also see that there is no exact linear behavior of the lattice parameters as expected from Végard’s law. The observed upward deviation in (Sm,Ca)VO$_3$ may just be coincidental.

We have demonstrated in Chapter 4 that Sm$_{1-x}$Ca$_x$VO$_3$ goes through an insulator to metal transition with increasing calcium concentration. For x=0.3 and x=0.4, the compound is an antiferromagnetic metal. The metallic behavior of the resistivity can be seen in Figures 5.1 and 5.2 and in particular the increase of resistivity due to weak localization at low temperatures.

At high temperature the conduction is dominated by itinerant electrons and the influence of the valence of the Sm ions may be only minimal. At low temperature, disorder leads to the weak localization resulting in an increase of the resistivity. Considering that we have a mixed valence state $\approx 2.5^+$, we offer two possible scenarios for the temperature-induced transition observed for x=0.3 and x=0.4:

- Charge ordering of Sm$^{2+}$ and Sm$^{3+}$,
- Lowering of the valence state to Sm$^{2+}$.

In the first scenario, the charge ordering of Sm$^{2+}$ and Sm$^{3+}$ combined with a mixed valence state of V$^{3+}$ and V$^{4+}$ would result in a decrease of the resistivity as observed in our measurements and should also be related to a lattice distortion. This scenario is quite likely due to the relatively small change in resistivity observed with temperature and the small change in transition temperature with magnetic field. Moreover, the Sm$^{3+}$ and Sm$^{2+}$ cations are in an approximately 1:1 ratio for both the x=0.3 and x=0.4 compositions. This ratio often favors charge ordering. Although charge ordering usually leads to an increase of resistivity as a gap opens, in our case the Sm cations are barely involved in the conductivity and a decrease in the scattering will lead to a decrease of the resistivity. Moreover, there are examples in the literature of charge ordering of rare-earths, the most relevant for this discussion being that of Sm cations in Sm$_4$Bi$_3$ [29].

In the second scenario, the lowering of the valence state to Sm$^{2+}$ would induce a change of valence of the V ions (involved in the conductivity) to V$^{4+}$. In that case, one may expect a much larger decrease of the resistivity than that observed. However, the presence of Ca$^{2+}$ may prevent a complete valence change to Sm$^{2+}$: the presence of the dopant being equivalent to applying pressure may prevent the large lattice expansion required by a total change of the valence state to Sm$^{2+}$. 
In that case the Sm valence state below the transition would be another mixed-valence state, although lower than that above the transition. However, in this scenario the origin of the temperature-induced transition remains unclear. We thus favor the first hypothesis related to charge ordering.

5.3.3 Magnetoresistance for x<0.3 or x>0.4?

One can consider the possibility of finding MR for lower calcium concentration, as we have shown that an intermediate valence state of Sm is also present for x=0.1 and x=0.2. Resistivity measurements could not be carried out down to the lowest temperatures for these compounds because of their large resistance. However, it strongly believed that such a transition would not occur for these concentrations. It has indeed been shown for example in (Sm,Gd)S [17] that if the doping level is outside a narrow range, no temperature-induced transition will take place. In our case, we do not observe MR for x=0.5 which hints that a mixed valence state does not guarantee a temperature-induced transition. When considering the proportion of Sm$^{3+}$ in the x=0.1 and 0.2 compounds and comparing it with x=0.3 and 0.4, we can assume that for the lower doping concentrations, no transition will be observed if a mixed valence state close to 2.5+ is the key to such a transition.

5.4 Conclusion

In Sm$_{1-x}$Ca$_x$VO$_3$, for x=0.3 and x=0.4, we observe a first order transition at low temperature, accompanied by a 20% decrease of the resistivity. No change in the type of conduction is observed, the system going from a weak localized state to a less weakly localized state. The transition is shifted toward lower temperature with increasing magnetic field because of the suppressed antiferromagnetic ordering of the Sm spins. The transition seems to be induced by temperature. The lowering of the resistivity can be ascribed to a decrease of the scattering induced by a charge ordering of Sm$^{2+}$ and Sm$^{3+}$ which are present in a 1:1 ratio.

5.5 Unresolved issues

The tentative explanation given above of the nature of the transition in Sm$_{1-x}$Ca$_x$VO$_3$ (x=0.3, x=0.4) requires more experimental work to confirm. We have included in the discussion possible origins of such a transition (and the resulting MR), and discarded what seems unrealistic. We are left with two hypotheses that can account for all of the experimental observations. Although we
favor the first hypothesis based on charge ordering of the Sm cations, further
evidence is needed in order to discard the second one. The charge ordering hy-
pothesis is mainly based on specific heat data revealing the mixed-valence state
of the Sm cations. It would be useful to use other techniques in order to probe
directly the valence state of the Sm ions, such as X-ray absorption near edge
structure (XANES) and X-Ray photoelectron spectroscopy (XPS).

In the diffraction data at room temperature for Sm$_{1-x}$Ca$_x$VO$_3$, we cannot
probe with accuracy the lattice changes arising from the mixed valence state of
the Sm ions. The decrease in the lattice parameters and associated unit-cell vol-
umes induced by the increasing metallic character of the compounds will dominate
any changes due to the valence state of Sm. However, for a given composition,
temperature dependent experiments could be performed, and it would be possible
to probe lattice changes induced by the expected crystal distortions. However,
high resolution may be needed and one should not forget that the transition ap-
ppears only below 8.5K for x=0.3. For the charge ordering scenario, the appearance
of superlattice reflections would be expected below the transition.

Pressure dependence experiments would also be enlightening. It is known
that applying external pressure will favor the oxidation of the Sm to a 3+ state
[17, 18, 21]. It would be interesting to perform simple resistivity measurements
under pressure to see the influence on the MIT as well as on the temperature-
induced transition at low temperatures for x=0.3 and x=0.4.
References


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