The recent interest in the field of transition metal oxides has largely been triggered by two major discoveries: high-temperature superconductivity and colossal magnetoresistance (CMR, see Section 1.4). In particular, there is a general tendency to study as many oxides with perovskite structures as possible. Perovskite-related compounds can display not only the two exciting phenomena mentioned above but also a wide range of other intriguing structural, magnetic and transport properties. The interplay among the orbital, spin and charge degrees of freedom in 3d transition-metal compounds is of major importance, and both theoretical and experimental studies are actively being performed in order to fully understand how these three parameters influence the properties of the compounds. When 3d transition-metal oxides are concerned, one may think that manganese oxides (Mn$^{3+}$: 3$d^4$, $t_{2g}^3$, $e_g^1$) would for example display a more extensive range of phenomena, thus leaving the vanadates (V$^{3+}$: 3$d^2$, $t_{2g}^2$, $e_g^0$) aside. Indeed, the Jahn-Teller effect is much stronger in compounds where the $e_g$ orbitals are partially filled such as the manganites, and coupling to the lattice dominates, as seen in phenomena such as charge and/or orbital ordering and/or disordering accompanied by a temperature dependent metal-to-insulator transition. As far as the $t_{2g}$ orbitals are concerned, the Jahn-Teller effect is weaker and so are the interactions between orbitals and lattice. However, the orbital ordering still has a dramatic influence on the physical properties. The last decade of research on vanadate perovskites
has shown that they are a very interesting system to study and that they exhibit extremely surprising properties. In this chapter, we shall give an overview on research done on vanadates so far and give an introduction to some of their structural and electronic properties.

1.1 The perovskite structure

The vanadate compounds studied in this thesis have an orthorhombic perovskite structure at room temperature with chemical formula RVO$_3$ (R= rare-earth, yttrium or divalent cation). The structure consists of corner sharing oxygen octahedra. The vanadium is located in the center of the octahedron, and the rare-earth cation is located between the octahedra (Fig. 1.1). The structure does not exhibit an undistorted cubic (space group Pm$\bar{3}$m) perovskite structure. Instead, the octahedra formed by the oxygen array are tilted, which distorts the structure to the orthorhombic space group Pbnm, with lattice parameters $a \approx b \approx c\sqrt{2}$. The distortion is necessary in order to accommodate cations that are too big or too small.

It is important to understand how this orthorhombic stabilization occurs, and more particularly how the crystal structure behaves upon calcium doping as carried out in Chapter 4. A useful parameter in this study is the tolerance factor as defined by Goldschmidt [1], which defines the size limit of the cation in order to achieve a stable perovskite. The formula for a composition RMO$_3$ is $t = \frac{(r_R + r_O)}{\sqrt{2(r_M + r_O)}}$, with $r_R$ the ionic radius of the R-site cation, $r_M$ the ionic radius of the M-site cation, and $r_O$ the ionic radius of O$^{2-}$. Geometry tells us that for $t=1$, one would obtain an ideal cubic perovskite (Pm$\bar{3}$m). However, it is still possible to obtain a stable perovskite under specific conditions [2, 3] for $0.75 < t < 1$.

The preferred coordination of the cations and a tolerance factor value between 0.75 and 1 do not guarantee the stability of the orthorhombic perovskite. The size of the vanadium cations also plays a major role. The ionic radius [4] of V$^{3+}$ (as well as that of V$^{4+}$ for the doped series) is above 0.51Å [2], allowing the vanadium to stabilize in octahedral coordination. A lower value would lead to the stabilization of a smaller ionic coordination.

The size of the R-site cation is also very important as its accommodation leads to extra stabilization. It should be large enough to stabilize in the proper coordination, but also small enough to allow a good optimization of the V-O bonding and prevent the formation of hexagonal stacking with face-shared octahedra that tends to occur for large R. It has been shown that the minimum radius of the R
1.1. The perovskite structure

Figure 1.1: Orthorhombic perovskite RVO$_3$.

cation is 0.90 Å, which our rare earths, yttrium and calcium cations obey [2]. The substitution of the R cation (R= rare-earth or Y) by the divalent calcium cation (in Chapters 4 and 5), which has a bigger ionic radius, increases the value of the tolerance factor for each series of R$_{1-x}$Ca$_x$VO$_3$ (Fig. 4.32). The tolerance factor, which also increases with the size of the rare-earth or yttrium, always remains below 1.

Vanadates satisfy most of the above prerequisites, as V$^{3+}$ prefers octahedral coordination, which leads to a stable VO$_3$ sublattice. The R-site cation (stable in 12-fold coordination) occupies the larger ionic interstice between the corner-shared VO$_6$ octahedra. As the tolerance factor is below 1, the V-O bonds are compressed while the R-O bonds are under tension. This stress is accommodated by the lattice by a slight rotation of the corner shared octahedra which leads to the stabilization of an orthorhombic structure. The buckling of the octahedra which allows the optimization of the R-O bond lengths results in an enlargement of the unit cell and a decrease of the V-O-V angle from 180°. These shifts of the oxygen atoms result in an energetically-favored shift of the R cation as to maximize the R-O covalency [5,6]. The pattern of rotations in all of the investigated compositions was the same, giving a structure that adopts the orthorhombic Pbnn space group.

It should be noticed that doping the trivalent rare-earth with the divalent calcium changes the mean valence on the vanadium site without changing the oxygen coordination. Upon doping, the value of the V-O-V bond angle increases and the structure becomes less distorted, as predicted from the tolerance factor values. We shall come back to this point in Chapter 4.
In \( \text{R}_{1-x}\text{Sr}_x\text{VO}_3 \) compounds \((r_{(\text{Sr}^{2+})} = 1.44 \text{ Å})\), temperature- and/or concentration-dependent transitions from orthorhombic to rhombohedral, orthorhombic to cubic, and tetragonal to cubic symmetry have been observed [7–9]. It was found to be very difficult (or even impossible) to achieve a perfect solid-solution for high doping concentrations of the much larger \( \text{Sr}^{2+} \) cation for small \( \text{R} \) [8, 9]. Moreover, different synthesis methods seem to lead to different results concerning the crystal structure as well as the homogeneity of the sample [7]. This illustrates how critical the tolerance factor (Fig. 4.32) and size of the cations are in the stabilization of an orthorhombic perovskite.

### 1.2 Jahn-Teller effect and orbital ordering

![Distribution of the electron density for the \( e_g \) orbitals.](image1)

![Distribution of the electron density for the \( t_{2g} \) orbitals.](image2)

In 1937, Jahn and Teller published their famous theorem [10] stating that:

“any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy.” From this statement, the Jahn-Teller (JT) effect was born and has been extensively studied for almost 70 years. JT ions are orbitally degenerate. When insulators are concerned, the JT effect can cause structural phase transitions, usually lowering the lattice symmetry and giving rise to an ordered occupation of orbitals. In a crystal with transition metal ions subject to the Jahn-Teller effect, the five-fold degenerate \( d \) level is split by the crystal field. In a field of cubic symmetry, the \( d \) level will split into a 3-fold degenerate level \( (t_{2g}) \) and a 2-fold degenerate level \( (e_g) \). The distribution of the electron density for the \( e_g \) and \( t_{2g} \) orbitals is represented in Figures 1.2 and 1.3 respectively. The \( t_{2g} \) level in octahedral coordination is of lower energy than the \( e_g \) level.
because the $t_{2g}$ orbitals form lower energy anti-bonding orbitals with the oxygen ligands. For $e_g$ levels, the orbital angular momentum is quenched. However, this is not the case for the $t_{2g}$ levels where the wave function may be characterized by an effective angular momentum $l_{eff}=1$ which leads to two possible mechanisms to lift the degeneracy: a JT mechanism and a spin-orbit mechanism. The main difference between the two is that a JT transition is structural and any possible magnetic ordering will generally occur at a different temperature. However, a transition determined by spin-orbit coupling goes together with magnetic ordering. This is extensively discussed by Kugel and Khomskii in reference [11]. In Figure 1.4 we present two possible types of JT distortion with the corresponding types of orbital ordering (OO) that are relevant for RVO$_3$. In Figure 1.5 one can see that in the G-type OO, the $d_{xy}d_{yz}$ and $d_{xy}d_{xz}$ orbitals are occupied alternately along all three directions, which corresponds to a bonding pattern with two pairs of short V-O distances and one pair of long V-O distances. The long V-O distance is caused by the overlap of the V $d$-orbitals with the O 2$p$ orbitals which gives rise to more electrostatic repulsion. The three V-O distances are arranged ”out of phase” (Fig. 1.4b) between successive $ab$ planes in the case of G-type OO. However, in the C-type OO, the $d_{xy}d_{yz}$ and $d_{xy}d_{xz}$ orbitals are occupied alternately in the $ab$ plane while the same orbitals are occupied along $c$. The ferro-arrangement of the orbitals along $c$ leads to an ”in phase” arrangement of the V-O distances in successive $ab$ planes (Fig. 1.4a).

![Figure 1.4](image1)

**Figure 1.4:**
Scheme of the distortion of the octahedra for: a) JT distortion associated with C-type OO; b) JT distortion associated with G-type OO.

![Figure 1.5](image2)

**Figure 1.5:**
Scheme of the occupied $zx$ and $yz$ orbitals (based on the cubic axes) for G-type and C-type OO; the axes show the orthorhombic reference system.

Chapter 3 will focus on the phenomenon of long-range OO arising from long-range elastic interactions of local JT distortions. We discuss the OO in vanadate compounds for which $t_{2g}$ orbitals are involved, study the related structural changes, and show how two types of OO can coexist under certain conditions.
1.3 Metal-insulator transition

In the late 1920’s, non- or weakly-interacting electron systems were considered in the early years of quantum mechanics [12–14]. Based on the filling of electronic bands, the theory predicted that:

- For metals, the highest band is partially filled, and the Fermi level is inside the band.
- For insulators, the highest band is completely filled, and the Fermi level is in the band gap.

A few years later, it was found that insulators with a small energy gap between the highest filled band and the lowest empty band would be semiconductors because of thermal excitations [15–18]. The success of these definitions ended when it was pointed out by de Boer and Verwey that many transition metal oxides with partially filled \(d\) electron bands (e.g. NiO) were found to be very poor conductors and often insulators [19]. An immediate reply to this report was made by Mott (in collaboration with Peierls) indicating that in fact electron-electron interactions may be taken into account to explain this behavior and that electrostatic interactions between the electrons may be responsible for such lack of conductivity. These two papers led to the ongoing research on strongly correlated electron systems, trying to understand the insulating state for partially filled bands. These insulators are known in a broad sense as Mott insulators after the extensive work of Mott on such compounds [20–23]. Moreover, it soon became of interest to understand why and how an insulator could become a metal: the metal-insulator transition (MIT).

The Hubbard model was used to investigate such a transition, describing one type of atomic orbitals [24–26]. Only the transition metal \(d\) orbitals are considered in this model. The charge excitation gap in this case is formed between the lower Hubbard band which is singly occupied and the upper Hubbard band which is doubly occupied. In some compounds, it was seen that the oxygen orbitals are also involved in charge transport. Indeed, orbital degeneracy sometimes leads the oxygen \(2p\sigma\) level to become close to (and sometimes even overlap) the partially filled \(3d\) band. The Zaanen-Sawatsky-Allen scheme (ZSA) [27] makes a distinction between these two types of insulating ground states: the charge-transfer insulator (CTI) where the electron correlation parameter, \(U\), is larger than the charge transfer energy, \(\Delta\); and the Mott-Hubbard insulator (MHI) for which \(\Delta > U\). Classification of the various types of metal-insulator transition has been revisited over the years through various theoretical approaches [23, 28], as
experimental results were brought in to show to what extent one model or the other should be used, due to the strong need to comprehend the metal-insulator transitions in strongly correlated compounds.

![Diagram](image)

**Figure 1.6:** Scheme after Imada *et al.* [28] showing that the MIT can be achieved by bandwidth control (BC-MIT) and filling control (FC-MIT).

Two routes can lead to the MIT: bandwidth control and filling control. In the Hubbard model, the electron correlation strength $U/t$ (where $t$ is the electron hopping term between non-interacting electrons) and the band filling $n$ are two parameters of importance. As can be seen in Figure 1.6, the MIT can be achieved by bandwidth-control which means that the MIT is driven by changing the $U/t$ parameter and will appear at a finite critical value, $U_c$. The electron correlation strength is controlled through the transfer interaction or the one-electron bandwidth ($W$) as the Coulomb interaction remains almost unchanged. Modifying $W$ is easily achieved by applying hydrostatic pressure as for example can be done for $\text{V}_2\text{O}_3$ [29] and $\text{RNiO}_3$ [30]. It is also possible to modify the chemical composition to achieve the MIT. As the electron correlation arises from a narrow $d$ band in transition metal compounds it is usual not to perform substitution on the transition metal cation site to control $W$. Other chemical sites are used, as for example in $\text{NiS}_2$, where the MIT is achieved by substituting S by Se in the solid solution $\text{NiS}_{2-x}\text{Se}_x$ [31, 32]. Often, $W$ is controlled by changing the ionic radius of the A site in $\text{ABO}_3$ perovskite compounds as can be done in $\text{RNiO}_3$ [33]. Although bandwidth control has been widely used, the discovery of high-temperature superconductivity in cuprates by band filling led to an extensive use of the filling control method for perovskite-type compounds because their structure can withstand significant chemical modification on the A-site.
Band filling in RMO$_3$ perovskites is usually achieved by substituting the rare-earth (or Y) by a divalent cation like Ca or Sr. Filling control can also be achieved by modifying the stoichiometry of the compound as for example in V$_{2-y}$O$_3$ [34] or LaTiO$_{3+y}$ [35].

In Chapter 4, we will present a detailed study of the nature of the metal-insulator transition in RVO$_3$ (R=Y, Sm, Pr). These compounds are Mott-Hubbard insulators as described in the ZSA scheme, and the MIT is achieved by band-filling control, i.e. hole doping. We will present structural, magnetic and transport properties of these compounds in order to study the nature of the MIT in these compounds.

### 1.4 Magnetoresistance

The change in resistance of a material under an externally applied magnetic field is known as magnetoresistance (MR). MR was discovered by Lord Kelvin in 1856 on a piece of iron whose resistivity increased by 0.033% under applied magnetic field [36]. This change in resistance in the bulk is due to the Lorentz-force, which causes extra deflection of the trajectories of the electrons [37,38]. This kind of MR depends on the orientation between current and field. The most common type of magnetoresistance is the anisotropic magnetoresistance (AMR) which depends on the orientation between current and magnetization. The magnitude of the change is very modest (usually of the order of 0.01% in a field of 1T) but AMR has found application in read-heads of magnetic recording devices and in magnetic proximity or motion sensors [39,40].

In 1988, a new kind of magnetoresistance was discovered in Fe/Cr/Fe multilayers [41]. The magnitude of this MR being very large, it was called giant magnetoresistance (GMR). As can be seen in Figure 1.7, different kinds of nanostructures can lead to GMR. Figure 1.7a. shows a magnetic multilayer structure built from thin ferromagnetic (FM) layers separated by a non-magnetic (NM) layer. The thickness of the NM layer is chosen specifically so that in the absence of an externally applied magnetic field, the magnetizations of adjacent FM layers are oppositely aligned. A strong enough external magnetic field will force the magnetization to align.
**Figure 1.7:** Various GMR nanostructures (left) and their magnetoresistive behavior [all horizontal scales are different] (right), adapted from Ref. [39]:

a. Antiferromagnetically coupled material
b. Spin-valve structure
c. Granular alloy
d. Hybrid nanostructure including clusters and layers.
A different kind of nanostructures exhibiting GMR are the so-called spin-valve structures. In this case the FM layers are of two different natures: each FM layer is composed of a type of material with a different coercivity to that in its neighboring FM layer. The FM layers with the larger coercivity are pinned to an external magnetic layer. The FM layers with smaller coercivity may be rotated on application of a small external magnetic field. The angle between the magnetic moments in the two FM layers controls the resistance of the device. In the absence of magnetic field, the relative alignment of the layers is controlled by the thickness of the non-magnetic layer. This phenomenon is represented in Figure 1.7b.

Multilayers are not easily prepared, and it is much easier to prepare granular alloys. For example in heterogeneous Cu-Co alloy films, the relative orientation of the magnetic moments in the Co-rich grains inside the Cu-rich matrix will determine the magnetoresistance, and it can be varied by an applied magnetic field [42]. One should note that GMR will not be observed in homogeneous alloys as they do not contain isolated large and magnetically-rich grains.

Hybrid materials including both layers and clusters are also engineered [43]. A record magnetoresistance of 6.5% per Gauss was obtained with such a structure. This kind of structure presents numerous advantages but the main drawback is the deterioration of the GMR at room temperature because of the crossover to superparamagnetic behavior. Thanks to GMR materials and more particularly to spin-valve structures, IBM has been able to produce a new generation of hard disk read-heads. GMR sensors are of extreme importance because they can be miniaturized, reproduced and manufactured.

The industrial need for materials presenting very large magnetoresistance at room temperature, and an ongoing need for more and more miniaturized devices makes the field of GMR structure of large importance. Just over a decade ago a new kind of very large magnetoresistance was discovered in perovskite-type manganites which revolutionized the world of magnetoresistive materials. The term giant being already used, these structures were said to exhibit colossal magnetoresistance (CMR). When for example the parent compound LaMnO$_3$ is doped with a divalent cation, the resulting compound is paramagnetic and insulating above $T_c$ but metallic and ferromagnetic below $T_c$. CMR arises when an applied magnetic field shifts the temperature of the metal-insulator transition. Extensive studies are being performed in order to fully describe CMR and the field is still under intensive research [44].

In addition to the typical AMR, GMR and CMR, various types of so-called anomalous magnetoresistance are being studied, arising from scattering and dif-
fert electronic and/or magnetic transition. We will present in Chapter 5 a large positive magnetoresistance found in (Sm,Ca)VO$_3$ at low temperature. The origin of this magnetoresistance related to weak localization effects, charge ordering and the mixed valence state of the Sm ions will be discussed extensively.

1.5 Short review of RVO$_3$ compounds

RVO$_3$ compounds (R= rare-earth or Y) have attracted researchers for more than fifty years now. In the last ten years, much has been reported experimentally and theoretically as the orbital ordering and interplay between orbitals and spins exhibited by RVO$_3$ compounds give rise to extremely intriguing physical properties.

1.5.1 The early days

Starting from 1954, the synthesis and structure of rare-earth vanadates has triggered quite some interest. Although the perovskite nature of the compounds was agreed upon, differences were initially reported in their structures. Eventually it was agreed that the compounds were orthorhombic and isostructural with GdFeO$_3$ [2,45–52,52–55], with a question mark for LaVO$_3$.

In the mid-1970’s the magnetic and transport properties were investigated [56–60], again with discrepancies in the reported results, until a systematic study was carried out by Sakai et al. [61], together with their Russian counterparts Zubkov, Bazuev and Borukhovich, mostly in the years 1973-1978. Weak ferromagnetism of the V-spins was reported, with the V$^{3+}$ spins oriented antiparallel by the isotropic exchange interaction but with a small canting caused by the antisymmetric exchange interaction [62–64]. Zubkov et al. had reported that both G- and C-type magnetic ordering were possible for vanadate compounds [58,65,66]. These magnetic orderings are analogous to the corresponding orbital orderings described in Section 1.2 and are characterized by an antiferromagnetic interaction in the $ab$ plane, but with a ferromagnetic interaction between the planes for the C-type, or an antiferromagnetic interaction between the planes for the G-type. Later on, the same authors carried out low temperature neutron diffraction measurements on all the vanadates (except Sm, Gd, Eu because of their strong absorption of neutrons). From this study, it was found that the beginning of the series (La to Dy) exhibited a C-type magnetic ordering whereas G-type was found at the end of the series (Y to Lu). YVO$_3$ was reported to be a special case because of a temperature-induced transition from G-type to C-type magnetic ordering [65]. Their report also contained a structural investigation. The C-type
magnetic compounds showed a structural phase transition near $T_N$ accompanied by a gradual change in the degree of orthorhombic distortion. For La and Ce, the transition was abrupt.

Sakai et al., who also reported on the magnetic properties of RVO$_3$ [61], measured the electrical conductivity of all RVO$_3$ (and Y) and found the vanadates to be extrinsic p-type semiconductors with an activation energy of about 0.1 eV. The resistivity was found to increase from La to Gd and to be almost constant between Tb and Lu. They ascribed their results to two main changes as the atomic number increases: the V-O-V bond angles deviate further from 180 degrees and an increase in the acidity of the rare-earth ions occurs (the more acidic, the more the R-cation competes for covalent mixing with the O$^{2-}$($p\pi$) orbitals which are active in the V-O-V interaction [67]). The effect of the acidity of the rare-earth ion was supposed to be the most significant [68].

### 1.5.2 Anomalous negative magnetization

In 1991, so-called field-cooled (FC) anomalous diamagnetism in LaVO$_3$ was reported for the first time [69, 70]. It could not be explained by core diamagnetism, Landau diamagnetism or superconductivity. The compound was found to undergo an increase in orthorhombic distortion just above $T_D$, the temperature where the magnetization becomes negative. This structural transition involves a large increase in structural anisotropy a few Kelvin below $T_D$. Similar anomalous properties were also observed below $T_l<T_N$ in CeVO$_3$ [71]. Many groups tried to explain this puzzling phenomenon [56, 59, 69, 70, 72–74], and it was first related to the orbital angular moment [74]. However, the current consensus is that it is due to the result of two coupled spin-canting mechanisms that oppose one another [75, 76]. The first mechanism is an antisymmetric exchange operating on a $c$-axis spin component, while the second mechanism corresponds to a magnetocrystalline anisotropy. In LaVO$_3$ and CeVO$_3$ the V-O-V bond angle is larger which weakens the antisymmetric exchanges, and the anisotropy term reverses the magnetization. In LuVO$_3$ and YVO$_3$, cooperative site rotation and a smaller V-O-V bond angle strengthen the effective antisymmetric exchange relative to the canting due to anisotropy [76].

Although LaVO$_3$ had previously been thought to be cubic or tetragonal, Geller et al. had mentioned already in 1957 that it should be orthorhombic (Pbnnm) at room temperature [77]. The first very precise structural study on LaVO$_3$ was reported by Bordet et al. and unveiled that LaVO$_3$ was indeed orthorhombic at room temperature (Pbnnm) and down to 140K [77]. Most previous studies failed to
detect the small distortion from cubic symmetry of LaVO$_3$. The most enlightening discovery by Bordet et al. was the transition to a monoclinic (P2$_1$/b11) structure below 140K which also explained the presence of two inequivalent V sites at low temperature in NMR measurements [78].

1.5.3 Phase transitions in YVO$_3$

In 1994, YVO$_3$ began attracting a lot of attention as Kawano et al. reported results opposing those of Zubkov et al. [65]. It was shown that YVO$_3$ possesses a G-type magnetic structure at low temperature (below 77K) and a C-type magnetic structure in the intermediate phase (77<T<114K). The transition between the two is accompanied by a lattice distortion. However, an orthorhombic (Pbnm) structure was reported for the whole temperature range studied. Another interesting feature of this report is that similarly to LaVO$_3$ [58], the saturated ordered magnetic moment is 20% lower than what would be expected for a S=1 spin-only system which was attributed to the presence of strong spin fluctuations.

Following the renewal of interest in 3$d$ transition metal oxides, the discovery of puzzling magnetic properties and a slightly better comprehension of the crystal structure, much theoretical work on the electronic structure was performed using various methods (LSDA, LDA+U, GGA) [79,80]. These band structure calculations were able to reproduce more or less accurately the ground states in YVO$_3$ and LaVO$_3$, the main problem arising mostly from a failure of these methods to reproduce properly the band gap. A different kind of calculation was also performed: Hartree-Fock calculation [81]. Taking into account the full degeneracy of the transition metal 3$d$ and oxygen 2$p$ orbitals and the onsite Coulomb and exchange interactions, this was able to reproduce more accurately the ground state properties of insulating oxides. Mizokawa and Fujimori presented in this report a full study on the relationship between the spin- and orbitally ordered compounds and the Jahn-Teller and GdFeO$_3$-distortions in RVO$_3$.

The discovery of a temperature-induced magnetization reversal in YVO$_3$ by Ren et al. [75] opened new doors in the study of the vanadates. An abrupt reversal of the magnetization at 77K ($T_s$) associated with a first-order structural phase transition was reported, and a gradual reversal around 95K which is not accompanied by a structural change was also observed. It should be noted that although the structural transition in LaVO$_3$ occurs just below $T_N$, in YVO$_3$ there is a wide temperature window between $T_N$ and $T_s$. Although various magnetic studies had been carried out on YVO$_3$, such behavior had not been previously observed due to a lack of data on single crystals. First of all it should be noted how unusual
temperature-induced magnetization reversals are. Reversal of the magnetization usually requires large magnetic fields: once aligned, the magnetic moment can be reversed by a large field in the opposite direction. However, temperature-induced magnetization reversal in a small field is a much more unusual effect and is generally seen in ferrimagnetic materials. In YVO$_3$, the net magnetic moment is caused by the canting of antiferromagnetically aligned V spins (which are crystallographically identical) due to the strong tilting of the octahedra. The oxygen ions mediating the superexchange interaction between two nearest V are not at an inversion center, so the antisymmetric Dzyaloshinsky-Moria (DM) interaction is also present, giving rise to a weak ferromagnetic moment in the opposite direction.

At the time of the publication, the authors had proof from single crystal diffraction that the OO is C-type at low temperature, leading to a G-type magnetic structure according to the Goodenough-Kanamori rules [82]. They also point out that the sudden change in the magnetic structure can lead to a change in the role of the DM interaction and anisotropy. Shortly after the publication of the results of Ren et al., similar results were presented by Nakotte et al., also on single crystals [83], and Ren et al. produced a more detailed report two years later [84].

Although YVO$_3$ was being extensively studied, little was done in order to check the structure above $T_N$, apart from the study by Kawano et al. [85] at 126K which revealed a Pbnm structure at this temperature. Through resonant X-ray scattering (RXS) at the V K-edge, Noguchi et al. could identify a change in OO from C- to G-type at $T_s$ via a first-order transition [86]. The authors also strongly suggested that long-range OO is present in the high temperature paramagnetic phase. However, they concluded that it could not be associated with JT distortion because it would violate the mirror symmetry normal to the c axis of the Pbnm lattice system. Although the use of RXS as a direct probe of OO is controversial [87–89], Takahashi et al. reproduced the results of Noguchi et al. using ab initio band-structure calculations based on the LDA where the lattice parameters from experimental work were used as input in the calculations [90,91].

The results of Noguchi et al. were confirmed while probing the OO indirectly: with synchrotron and neutron diffraction. Blake et al. reported that indeed G-type OO above $T_N$ was present in YVO$_3$ [6,92], until 200K. The change in type of OO at 77K was manifested by a change in the type of JT distortion and was caused by increasing octahedral tilting with decreasing temperature [5]. The structure was shown to be monoclinic in the G-type OO phase. The transitions observed by Blake et al. were perfectly reproduced by Marquina et al. [93] while performing lattice expansion and magnetostriction experiments on a single crystal. The magnetostriction results revealed the stability of the low-temperature-magnetic
ground state under very high magnetic field (30T). The authors could prove in this way that the thermal expansion technique is a very powerful tool to detect the transitions in YVO$_3$, and the same kind of investigations were later carried out on other vanadates [94].

De Silva et al. [95] studied the electronic structure of YVO$_3$ and derived the effective Hamiltonian based on superexchange and could reproduce the results of Blake et al.. Studying the classical solution within mean-field theory, they found that this theory explained well the orbital and spin ordering for T > 77K but could not explain the lower temperature phase of G-type spin ordering.

Further details of the phase between 77K and 200K were obtained by Tsvetkov et al. who carried out an optical and magneto-optical study of the orbital and spin ordering transition, in the IR, visible, and UV regions [96, 97]. In a short first report they confirmed a lowering of the symmetry below a second-order phase transition at 200K. The main difference with the report of Blake et al. lies in the structure below the ordering temperature. From the phonon spectrum, Tsvetkov et al. demonstrated a lowering of the symmetry toward either a monoclinic Pb11 or triclinic P1 structure.

Around that time, first principle studies on the anisotropic optical conductivities due to spin and OO were carried out by Fang et al. in LaVO$_3$ and YVO$_3$, which cast doubt on the previous results [98]. The research led by the authors was triggered by the fact that anisotropy of low energy (below 5 eV) optical excitations in strongly correlated transition metal oxides is closely related to spin ordering and OO and the success of the LDA+U calculations in vanadates. Their calculations could reproduce the experimental optical conductivity spectra of both LaVO$_3$ and YVO$_3$ at low temperature obtained by Miyasaka et al. [99]. However, for the intermediate phase (for YVO$_3$), the calculation suggested that 50% of the low-temperature phase remains.

Following the studies of the OO transitions in YVO$_3$, Miyasaka et al. published a systematic study of these transitions in most RVO$_3$ using specific heat measurements as a tool [100]. This allowed the authors to compose a phase diagram which is the current reference for all transitions in the vanadates. They found that with increasing lanthanide ionic radius, $T_N$ increases while the onset temperature of the OO increases from Lu to Gd then decreases for the larger ions. Some doubts remain on the interpretation of the results for LaVO$_3$ and CeVO$_3$. A report by Ren et al. in 2003 presents the specific heat and single crystal diffraction data [101]. For LaVO$_3$ a second order transition was observed at $T_N$=143K and a first order transition at $T_t$=141K. In CeVO$_3$, they find a second order transition at $T_O$=154K and a first order transition at $T_N$=134K. The authors
propose that for CeVO$_3$ the structure change at $T_N$ is due to an OO-enhanced magnetostrictive distortion. The onset of OO in CeVO$_3$ would then be above $T_N$, contrary to the report of Miyasaka et al. For LaVO$_3$, Ren et al. propose that the first-order transition at $T_f$ should be associated with a sudden change in both spin and orbital configurations.

1.5.4 Quantum versus Jahn-Teller orbital physics

Currently, the main debate in the vanadates involves a description of the low energy physics. In 2001, Khaliullin et al. proposed a quasi-1D spin-orbital model [102] which is at the origin of the discussion. In this paper it was shown that strong $t_{2g}$ quantum orbital fluctuations in a half-filled system of $yz$ and $zx$ orbitals in RVO$_3$ are necessary in order to stabilize the stronger than expected ferromagnetic superexchange along the $c$-axis in the C-type magnetic phase. In this scenario, there should be no JT distortion together with the C-type magnetic phase. However, the JT effect would still stabilize the G-type magnetic phase (with C-type OO) at low temperatures. When orbital fluctuations dominate and there is no JT distortion at all, Khaliullin et al. have predicted that orbitals should dimerise along the $c$-axis to give a so-called orbital Peierls state. Evidence for an orbital Peierls state [103–105], where orbitals are dimerised along the $c$-axis, was obtained by magnetic neutron scattering by Ulrich et al. in YVO$_3$ [106]. This state would be consistent with Pb11 symmetry, as previously observed by Tsvetkov et al. [97]. In the C-type magnetic phase the magnon band width along the FM $c$-axis was larger than that in the antiferromagnetic $ab$ plane. This violates the classical Goodenough-Kanamori rules stating that FM superexchange interactions are generally substantially weaker than AFM interactions [82]. These observations were analyzed using the quasi-1D spin-orbital model, which successfully explains most of the unusual features of the $T_s < T < T_{oo}$ phase of YVO$_3$. Most subsequent theoretical studies of YVO$_3$ and LaVO$_3$ using this model support its validity [99, 107, 108].

Whether the lifting of the degeneracy of the $xz/yz$ orbital doublet is controlled by superexchange or is of lattice origin remains controversial. Theoretical and experimental work would seem to favor the superexchange mechanism [109]. Lattice dimerization has so far not been observed in diffraction experiments, but this may be rendered difficult by the weak lattice coupling of the $t_{2g}$ orbitals as well as the large thermal and quantum fluctuations [106]. Thermal conductivity experiments

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1 A review on this matter has been published: G. Khaliullin, Progress in Theoretical Physics, Supplement, 160, (2005)
on vanadate single crystals show that in the room temperature phase, above the OO temperature, the crystals conduct like a glass [110]. The phonon contribution to the thermal conductivity is only partially restored by OO because of spin-phonon scattering, which decreases greatly below $T_N$. A first-order transition to a phase with much higher thermal conductivity is observed for $R<$Dy below the transition from C-type to G-type magnetic ordering. Khaliullin reports that these results are consistent with the orbital fluctuations model [109]. Several reports, however, suggest that Jahn-Teller orbital physics should not be discarded when explaining the properties of the G-type OO phase [111, 112]. They argue that JT distortions will lift the orbital degeneracy and suppress the quantum orbital fluctuations. They emphasize that the observed Jahn-Teller distortions [6, 86, 92] are in fact strong in these compounds and should not be neglected. Fang et al. [112] reproduced the magnon spectra of Ulrich et al. [106] by taking into account inequivalent VO$_2$ layers. The large difference between the exchange coupling strength in consecutive layers would arise from different magnitudes of JT distortions in the two layers. Their calculations show that the unusual magnetic properties of LaVO$_3$ and YVO$_3$ can be explained using a JT picture. However, optical experiments reveal a smaller JT coupling [99]. Whether quantum or Jahn-Teller orbital physics should be chosen to explain the properties of the vanadates remains uncertain, and more experimental work needs to be performed. We shall come back to this point in Chapter 3.

### 1.5.5 Some other works

Other interesting reports have been published on rare-earth vanadates. It has been reported for example that photoexcitation can melt the OO in LaVO$_3$ [113, 114]. Tsvetkov et al. reported a large Kerr rotation below $T_s$ in YVO$_3$ comparable to those in ferromagnets [97]. Studies of the magnetic properties of SmVO$_3$ [115, 116], and PrVO$_3$ [64, 117, 118] have been reported. The study by Tung [118] on PrVO$_3$ single crystals is noteworthy as it reveals a staircase-like behavior in the FM hysteresis loop below 3K. This behavior was reported to be related to avalanches of domain flips and the presence of random fields that could be generated in the quantum orbital fluctuation model presented by Khaliullin [109]. The same author also reported temperature-induced magnetization jumps in the AFM GdVO$_3$ below 8K [119]. The magnetic state at low temperature was found to be history dependent, the memory effect suggesting the presence of different domain arrangements. Coming back to YVO$_3$, Massa et al. presented results on polycrystalline samples concerning the phonon activity [120]. Based on IR spectroscopy and EX-
AFS, they suggest that an incommensurate structural phase exists between 77 and 210K due to competing ordering mechanisms.

Rare-earth vanadate compounds reveal a range of extremely interesting properties and still need to be carefully investigated experimentally and theoretically. We will present in the following chapters of this thesis some unusual behavior such as competing orbital orderings, the nature of the metal-insulator transition upon hole doping and large positive magnetoresistance.
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