Chapter 4

Jahn-Teller phase transitions in rare-earth manganites

4.1 Introduction

The rare-earth perovskites RTMO$_3$, with R a rare-earth element and TM a transition metal, have been intensively studied because of their large variety in physical phenomena such as superconductivity, ferroelectricity and colossal magnetoresistance. In all these phenomena, the electronic properties are intimately related to the lattice. Many of the interesting phenomena involve a complex interplay between the spin, charge, and orbital degrees of freedom, accompanied with subtle displacements in the crystal lattice.

In this chapter we will focus on the evolution of the orbital ordering and its relationship with the insulator to metal transition. In the perovskite manganites RMnO$_3$ the Mn$^{3+}$ ion has a $d^4$ configuration. In octahedral symmetry, the $d$ levels split into $t_{2g}$ and $e_g$ orbitals. The Mn$^{3+}$ ion has high-spin configuration (schematically presented in Fig. 4.2(b)), with three electrons occupying the three $t_{2g}$ orbitals and one electron occupying the doubly degenerate $e_g$ orbitals as $t_{2g}^3 e_g^1$. According to the Jahn-Teller (JT) theorem, the structure will distort thereby removing the degeneracy of the $e_g$ orbitals. In solids, the orbital degree of freedom of the Mn$^{3+}$ ion often shows long range ordering associated with the cooperative JT effect.

It is observed for the most extensively studied compound throughout the RMnO$_3$ series, i.e. LaMnO$_3$, that below a transition temperature $T_{JT}$, the 3$d_{3z^2-r^2}$ and 3$d_{3y^2-r^2}$ orbitals are ordered in the $ab$ plane in an alternating fashion. The transition to a disordered phase with fluctuating local JT distortions takes place at much higher temperature ($T_{JT} \approx 800$ K) than the antiferromagnetic transition temperature ($T_N = 140$ K). The structural evolution with temperature studied with x-ray and neutron diffraction techniques [1, 2] shows a transition from the O'-orthorhombic phase to a cubic
or a O*-orthorhombic phase attributed to the orbital order-disorder transition (at $T_{JT}$) followed by a second structural transition to rhombohedral symmetry (at $T_2$). Although the presence of the two structural transitions was well established by the authors of Ref. 1 and Ref. 2, the reported symmetry for the intermediate phase differs (cubic in Ref. 1 and orthorhombic in Ref. 2). Furthermore, the transition temperatures in the two reports do not coincide: $T_{JT} \approx 600$ K and $T_2 \approx 800$ K in Ref. 1 and $T_{JT} \approx 800$ K and $T_2 \approx 1000$ K in Ref. 2. The lower transition temperatures could be a result of the introduction of non-JT active Mn$^{4+}$ ions ($d^3$ configuration) due to the formation of the oxidized state LaMnO$^{3+}_3$ during the synthesis or during the high temperature measurements.

![Figure 4.1](image)

Figure 4.1: (a) Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ near the ferromagnetic insulator (FMI) - ferromagnetic metal (FMM) transition taken from Ref. 3. The shaded area indicates the orbital order (O') - orbital disorder (O*) transition region. (b) Magnetic and structure phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ taken from Ref. 5. The squares and circles denote the onset of the ferromagnetic and antiferromagnetic components, respectively, while diamonds denote rhombohedral to orthorhombic phase transition temperatures. The triangles indicate the structural phase transition observed in the $x = 0.125$ sample.

The studies of doped LaMnO$_3$ showed that the increase of the concentration of non-JT active Mn$^{4+}$ ($d^3$ configuration) by doping with Ca or Sr reduces the orbital order-disorder transition temperature [3, 4]. For critical concentrations of 21% Ca and 12.5% Sr, respectively, the cooperative JT distortion is completely suppressed. The low doping region of the phase diagram for LaMnO$_3$ - LaCaO$_3$ (taken from Ref. 3) and LaMnO$_3$ - LaSrO$_3$ (taken from Ref. 5) is represented in Fig. 4.1(a) and 4.1(b).

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† Here we take the phase diagram for LaMnO$_3$ - LaSrO$_3$ from Ref. 5, as it permits an easy comparison with the LaMnO$_3$ - LaCaO$_3$ phase diagram taken from Ref. 3. However, the phase diagram for LaMnO$_3$ - LaSrO$_3$ has been studied in much more detail by the authors of Ref. 6.
4.2 Crystal structure of RMnO$_3$ perovskites

The perovskite RMnO$_3$ structure consists of corner sharing octahedra, with the Mn ion in its center and the R occupying the holes between the octahedra. At high temperatures, most of the RMnO$_3$ perovskites are cubic. The undistorted cubic parent structure is schematically depicted in Fig. 4.2(a).

However, the small radius of the R ion compared with the voids between the octahedra will result at RT in a cooperative buckling and tilting of the corner-shared octahedra such that RMnO$_3$ perovskites structures distort to orthorhombic $Pbnm$ symmetry. These distortions manifesting in cooperative rotations of the octahedra are known as the GdFeO$_3$ distortions.

†† Although yttrium is not a rare earth it forms a stable trivalent cation with a similar ionic radius to those of the smaller rare earth ions.
Besides the rotation, the \textit{Pbnm} symmetry allows also a JT distortion of the octahedra. As already discussed in the Section 4.1, the JT effect originates from the high spin $d^4$ configuration of the Mn$^{3+}$ ions with one electron occupying the doubly degenerate $e_g$ orbitals (as schematically depicted in Fig. 4.2(b)).

![Figure 4.2: (a) The cubic perovskite unit cell. The La, Mn, and O ions are represented by black, grey and open circles. (b) The crystal field splitting in an octahedral environment.](image)

The orthorhombic \textit{Pbnm} symmetry is obtained from the undistorted cubic perovskite structure by rotations of the octahedra in antiphase about the pseudocubic $a$ and $b$ axis and in-phase about the pseudocubic $c$ axis. The in-phase and antiphase rotations are denoted by Glazer [13] with the superscripts + and - respectively, such that the symbol associated with the \textit{Pbnm} space group is $a^{-}a^{-}b^{+}$ ($a$ and $b$ refers to the pseudocubic subcell). There are two types of distortions associated with the JT effect: Q2 and Q3. The Q3 is a tetragonal distortion which results in an elongation or a contraction of the MnO$_6$ octahedron corresponding to the filled $3z^2 - r^2$ orbital or $x^2 - y^2$ orbital, respectively (Fig. 4.3(a) and 4.3(b)). The Q2 is an orthorhombic distortion (Fig. 4.3(c)) obtained by a certain superposition of the $3z^2 - r^2$ and $x^2 - y^2$ orbitals. [14, 15]

In a mathematical description, the operators $T_i$ of the pseudospin 1/2 describe the orbital occupation, such that $T^z = 1/2$ corresponds to the occupied orbital $3z^2 - r^2$ and $T^z = -1/2$ corresponds to the occupied orbital $x^2 - y^2$. The Q2 distortion corresponds to a pseudospin operator $T^x$. Thus, an arbitrary distortion described by a linear superposition of the wave functions is characterized by the angle $\theta$ in the ($T^x$, $T^z$) plane (Fig. 4.3(d)). The bonding ($\psi_g$) and antibonding ($\psi_e$) orbitals are obtained as the linear combinations $\psi_g = c_1\phi_{x^2-y^2} + c_2\phi_{3z^2-r^2}$ and $\psi_e = c_1\phi_{x^2-y^2} - c_2\phi_{3z^2-r^2}$. The

††† Instead of the standard setting \textit{Pnma} we use the \textit{Pbnm} setting for consistency with most of the listed citations. In the \textit{Pbnm} notation, the symbol $b$ denotes a glide plane perpendicular to the $a$ axis with a glide vector $1/2b$; the $n$ glide plane is a glide reflection through a plane $\perp [010]$ with the glide vector $1/2(a+c)$; the symbol $m$ denotes a mirror plane perpendicular to the $c$ axis.
4.2. Crystal structure of RMnO$_3$ perovskites

Figure 4.3: (a) and (b) The Q3 distortion with oxygen displacements corresponding to the filled $3r^2 - z^2$ and $x^2 - y^2$ orbitals, respectively. (c) The Q2 distortion which stabilizes a certain superposition of $3r^2 - z^2$ and $x^2 - y^2$ orbitals. (d) $(T^z, T^x)$ plane in which JT distortion can be described.

coefficients $c_1$ and $c_2$ which satisfy the condition $c_1^2 + c_2^2 = 1$ can be obtained from the equations: $\tan(\theta) = Q2/Q3$ and $\tan(\theta/2) = c_1/c_2$. The distortion modes characterizing the JT effect are defined as: $Q2 = 2(l - s)/\sqrt{2}$ and $Q3 = 2(2m - l - s)/\sqrt{6}$ with $l$ and $s$ the Mn-O distances in the $ab$ plane and $m$ the out of plane Mn-O bond length. [14, 15]

The oxygen framework is described in $Pbnm$ symmetry by two oxygen positions: the O$_1$ position situated on the mirror plane and attributed to the out-of-plane oxygens; the O$_2$ position attributed to the in-plane oxygens (see Fig. 4.4). The rotations of the octahedra are reflected in the deviation from $180^\circ$ of the Mn-O-Mn tilting angle. The JT effect in LaMnO$_3$ is dominated by the Q2 distortion with alternating long ($l$) and short ($s$) Mn-O$_2$ bond lengths in the $ab$ plane and a medium out of plane Mn-O$_1$ ($m$) bond length (see Fig. 4.4). The medium bond length $m$ deviates from the average bond length, such that $m < (l + s)/2$, indicating that the JT distortion is not of a pure Q2 type. A contribution of the Q3 distortion is also present. Thus the distortion of the octahedra is defined such that the deviation of the Mn-O distances with respect to the average $<d>$ value is quantified: $\Delta = (1/6) \sum_{n=1,6}(d_n - <d>/ <d>)^2$ [15].

The distortion to orthorhombic $Pbnm$ (with the unit cell parameters denoted by $a_O$, $b_O$ and $c_O$) will enlarge the original cubic cell ($a \approx 3.9$ Å), such that $a_O \approx b_O \approx \sqrt{2}a$ and $c_O \approx 2a$. There are two substructures having orthorhombic symmetry with the space group $Pbnm$, denoted as O- and O'-orthorhombic structure, respectively. The O-orthorhombic structure is due to the cooperative buckling of the corner-shared octahedra (pure GdFeO$_3$ rotation). The O'-orthorhombic structure is only found where a cooperative JT distortion is superimposed on the O-orthorhombic structure [16, 17].
Figure 4.4: (a) The JT distorted perovskite structure (the rotation is not indicated). The cubic and orthorhombic unit cells are indicated by thin and thick contours respectively. (b) The ab plane highlighting the alternation of the short and long Mn-O distances in a and b directions.

A criterion can be established for distinguishing between the O'- and O-orthorhombic structures, by comparing the $a_O$ and $c_O/\sqrt{2}$ orthorhombic unit cell parameters. Thus, for the O-orthorhombic structure, due to the pure rotation of the octahedra, $c_O/\sqrt{2} > a_O$ and $a_O < b_O$. For the O'-orthorhombic structure a cooperative JT distortion with $m < (l + s)/2$ superimposes on the rotation of the MnO$_6$ octahedra. By relating the short, medium and long Mn-O distances (obtained from the JT distortion of the MnO$_6$ octahedra) to the orthorhombic $a_O$ and $c_O$ unit cell parameters (see Fig. 4.4), i.e. $a_O = \sqrt{2}a = \sqrt{2}(l + s)$; $c_O = 2a = 4m$, the relation between the unit cell parameters for the O'-orthorhombic structure becomes: $c_O/\sqrt{2} < a_O < b_O$.

The RMnO$_3$ with large ionic radii (from La to Eu), crystallize with the perovskite structure having at RT O'-orthorhombic Pbnm symmetry. For rare-earth manganites smaller than Tb, the orthorhombic perovskite structure is no longer the stable phase under ordinary synthetic conditions since the hexagonal non-perovskite phase strongly competes in stability. Nevertheless, as shown for YMnO$_3$, the transition to the metastable orthorhombic phase can be stabilized by high pressure synthesis or by changing the average ionic radius of the R site, i.e. by partial substitution of Y with Gd or Ca [18]. Remarkably, for the non-JT distorted RFeO$_3$ series with the size of
Fe$^{3+}$ ($d^5$ configuration) similar to the size of Mn$^{3+}$ ($d^4$ configuration), the perovskite structure is stable for all the R ionic sizes, i.e. from La to Lu. Thus, the instability of the perovskite structure for small R ions in RMnO$_3$ is probably a consequence of the interplay between the rotation and JT distortion in these compounds.

4.3 Experimental

Polycrystalline samples of NdMnO$_3$ and Y$_{1-x}$Ca$_x$MnO$_3$ were prepared by a conventional solid-state reaction. The starting materials for NdMnO$_3$ are Nd$_2$O$_3$ and MnO$_2$ and for Y$_{1-x}$Ca$_x$MnO$_3$ are Y$_2$O$_3$, CaCO$_3$ and MnO$_2$. Stoichiometric amounts of the starting materials were mixed according to the following reactions:

$$\text{Nd}_2\text{O}_3 + 2\text{MnO}_2 \rightarrow 2\text{NdMnO}_3 + 1/2\text{O}_2$$

$$(1 - x)\text{Y}_2\text{O}_3 + 2x\text{CaCO}_3 + 2\text{MnO}_2 \rightarrow 2\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3 + 2x\text{CO}_2 + (1 - x)/2\text{O}_2$$

The rare-earth sesquioxides (i.e. R$_2$O$_3$) being very sensitive to the carbon dioxide and moisture (formation of R$_2$(CO$_3$)$_3$.3H$_2$O), were dried before use at $1000^\circ$C overnight. The mixtures of the starting materials were weighted in stoichiometric amounts and ground thoroughly in an agate mortar. The obtained powders were heated in air at $1200^\circ$C overnight. This procedure was repeated twice for Y$_{1-x}$Ca$_x$MnO$_3$ with an intermediate grinding to improve the crystallinity of the samples. For the NdMnO$_3$ sample, in order to avoid the formation of undesirable Mn$^{4+}$ (production of oxidized NdMnO$_{3+\delta}$ phase), the heating process was done in nitrogen atmosphere. The Y$_{0.8}$Ca$_{0.2}$MnO$_3$ single crystal was grown by the floating-zone technique in an image furnace.

The SXD measurements were performed on a small single crystal fragment of approximate dimension 0.1 mm. Full data sets were measured at 100 K and 295 K on a Bruker APEX diffractometer equipped with a two dimensional detector and using Mo-K$_\alpha$ radiation. The integration of the frames was carried out using the SAINT [19] software incorporating the absorption correction program SADABS. Structural determination and refinement was carried out using the SHELXTL [20] package. The presence of twinning was checked using an Enraf-Nonius CAD4 diffractometer equipped with a point detector. The temperature dependence PXD experiments were performed on a Bruker-D8 diffractometer, using Cu-K$_{\alpha 1}$ radiation and a step size of $2\theta = 0.04^\circ$ with 30 sec./step. The PXD experiments at RT for different Ca concentrations in Y$_{1-x}$Ca$_x$MnO$_3$ samples were performed on a Philips diffractometer using Cu-K$_{\alpha 1}$ and Cu-K$_{\alpha 2}$ and a step size of $2\theta = 0.04^\circ$ with 20 sec./step. The PXD data were analyzed by the Rietveld method using TOPAS [21]. The resistivity was measured using a standard four-point
method using an Agilent 3458A measure unit.

4.4 High temperature structural transition in NdMnO$_3$

NdMnO$_3$ is a member of the RMnO$_3$ series with a stable perovskite structure. The RT structure is O’-orthorhombic $Pbnm$ with a large JT distortion of the octahedra. The size of the Nd ion close to the average value between the large La and small Er, places the rotation (the deviation of the $<\text{Mn-O-Mn}>$ angle from 180°) of NdMnO$_3$ close to the average value of the rotation between the LaMnO$_3$ rotation and the ErMnO$_3$ rotation [7].

We study the high temperature behavior of NdMnO$_3$ by performing PXD experiments in air and in vacuum in the temperature interval 300 K - 1473 K. As discussed in the Section 4.2, the transition from the O’-orthorhombic structure to O-orthorhombic structure is expected to be identified in the temperature evolution of the lattice parameters.

The structural refinement at RT was performed in the $Pbnm$ space group using as a starting point the structural parameters taken from the Ref. 7. The small oxygen displacements (due to changes in rotation and JT distortion) and the Debye-Waller factors have the largest influence on the intensities of the weak peaks of the powder patterns. The measured intensity to background ratio of these peaks is low, leading to difficulties in separating the contribution of the oxygen movement from the contribution of the Debye-Waller factors. Therefore we can not accurately refine the oxygen positions for a quantitative determination of the bond lengths and angles and implicitly of the JT distortion parameter and rotation parameter.

The peaks could be indexed in the $Pbnm$ symmetry at all temperatures. Regardless the precise refinement of the oxygen fractional coordinates, the positions of the peaks and implicitly the lattice parameters can be refined with high accuracy due to the high angular resolution of the PXD technique. Thus we performed our refinements by fixing the oxygen positions at the RT values taken from Ref. 7 and by refining the following parameters: scale factor, background coefficients, zero-point error, unit cell parameters and Gaussian parameters. The peak profiles were very well reproduced by the used Gaussian peak shape. For all the measured patterns, the refinements proceeded smoothly, giving no indication for considering a different symmetry.

From the evolution of the lattice parameters, the structural change from the orbitally ordered O’-orthorhombic structure (with $c/\sqrt{2} < a < b$) to the orbital disordered O-orthorhombic structure (with $a < c/\sqrt{2} < b$) can be easily identified. Thus, for the measurements performed in air, the temperature dependence of the lattice parameters $a$, $b$ and $c/\sqrt{2}$ and of the cube
4.4. High temperature structural transition in NdMnO$_3$

Figure 4.5: Temperature dependence of the NdMnO$_3$ unit cell parameters measured in air. The lines are guides for the eye. The shaded area indicates the region in which the O'-orthorhombic phase (filled symbols) and O-orthorhombic phase (open symbols) coexist.

Root of the molecular volume $\sqrt[3]{V}$ depicted in Fig. 4.5 show the presence of the O'-orthorhombic phase (filled symbols) up to 973 K, the coexistence of the O'- and O-orthorhombic phase for T = 1073 K and 1173 K and the pure O phase (open symbols) at T = 1273 K. This structural transition can be directly identified in the powder diffractograms (see Fig. 4.6) by the dramatic change in the refined peak positions from 973 K to 1273 K. The positions of (0 2 1) and (2 0 0) reflections are reversed with increasing temperature from 973 K to 1273 K as a result of reversing the ratio between the lattice parameters, i.e. from $c/\sqrt{2} < a$ to $c/\sqrt{2} > a$. The patterns collected at intermediate temperatures, i.e. 1073 K and 1173 K, show the presence of peaks belonging to both O'- and O-orthorhombic structures, indicating the coexistence of both phases in this temperature interval. By increasing the temperature from 1073 K to 1173 K, the peaks intensities corresponding to the O-orthorhombic structure increase on the expense of the decreasing of the peaks intensities corresponding to the O'-orthorhombic structure. The diffraction patterns at 1073 K and 1173 K were refined by including both phases (in Fig. 4.5, at 1073 K and 1173 K, the lattice parameters of both phases are indicated). The refined ratio between the O'- and O-orthorhombic phase at the 1073 K and 1173 K changes from 2:1 to 1:2, respectively, suggesting a two phase region. The discontinuity in the temperature dependence of the lattice parameters and of the molecular vol-
ume at the transition between the two phases suggests a first order phase transition.

The structural phase transition is attributed to the orbital order-disorder transition occurring over a temperature interval $\approx 1000\,\text{K} < T < 1200\,\text{K}$. The coexistence of the O'- and O-orthorhombic phases over a temperature interval is in agreement with an earlier structural study [9]. Furthermore,
recent transport measurements [23] observed a large drop of the thermoelectric power over a temperature interval denoted by the authors as $T^* < T < T_{JT}$. The two regimes, i.e. $T < T^*$ and $T > T_{JT}$, are interpreted with a cooperative JT ordering of the occupied $e_g$ orbitals of the MnO$_6$ octahedra and short range orbital fluctuations, respectively. The differences in the transition temperature intervals reported in these studies, i.e. 873 K $< T < 1023$ K [9] and 800 K $< T < 1123$ K [23] can be a result of the Mn$^{4+}$ impurities due to deviation from stoichiometry, especially increased oxygen content during the synthesis or during the high temperature measurements in air. By increasing the oxygen content, non-JT active Mn$^{4+}$ ions are introduced leading to the reduction of the orbital order-disorder transition temperature. The coexistence of the O'- and O-orthorhombic phases over a temperature interval was also observed for PrMnO$_3$ [10] and SmMnO$_3$ [9]. There is no structural study indicating such a phase coexistence for LaMnO$_3$. However, in La$_{1-x}$Ca$_x$MnO$_3$ with $x = 0.16$ and $x = 0.19$ the temperature evolution of the JT distortion parameter indicates the coexistence of the O'- and O*-orthorhombic phases [3]. The authors of Ref. 3 observed that the width of the temperature interval in which the two phases coexist decreases with decreasing $x$ and probably becomes very small for $x = 0$. This explains why the phase coexistence was not identified in LaMnO$_3$.

We analyzed the effect of the Mn$^{4+}$ ions on the JT transition by comparing the measurements performed in air with measurements performed in vacuum ($10^{-2}$ mbar). In order to check the actual temperature of the sample in the two media, we consider as a reference the platinum stripe used as a sample holder for the high temperature measurements. We observe that the temperature evolution of the lattice parameters of the platinum in both air and vacuum is the same within the standard deviations. This shows that for the same set temperature points in air and in vacuum, the actual temperatures of the sample in the two media are equal. We notice that in vacuum, the orbital order-disorder transition in NdMnO$_3$ occurs in the temperature interval 1200 K - 1400 K which is 200 K higher than the one resulted from the measurements in air. This result is evidence that the measurements in air probe an oxidation phase NdMnO$_{3+\delta}$ with $\delta \approx 0.2$ which introduces non-JT active Mn$^{4+}$ ions. Although our results indicate that the measurements performed in vacuum avoid the formation of the Mn$^{4+}$, we will continue to refer to the transition interval resulted from the measurements performed in air. This allows us to compare our results to the reports in the literature [2, 9, 10].

As our data does not allow the refinement of the fractional coordinates of the oxygens, we can not determine the temperature evolution of the magnitude of the rotation and JT distortion. However, from the evolution of the unit cell parameters we can estimate that similar to LaMnO$_3$ the JT parameter decreases to zero at the temperature at which the orbital
ordering is completely suppressed, i.e. 1273 K. The large difference between the \(a, b\) and \(c/\sqrt{2}\) at 1273 K indicating a large rotation parameter above the transition is in contrast with the result obtained above \(T_{JT}\) in \(\text{LaMnO}_3\) with \(a \approx b \approx c \sqrt{2}\) \cite{1, 2}. This difference can be ascribed to the smaller ionic radius of \(\text{Nd}^{3+}\) than of \(\text{La}^{3+}\).

4.5 Jahn-Teller phase transitions in \(\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3\)

The small ionic radius of \(\text{Y}^{3+}\) results in a small value of the tolerance factor\(\dagger\) leading to instability of the perovskite structure. \(\text{YMnO}_3\) and all \(\text{RMnO}_3\) with \(\text{R}^{3+}\) ion smaller than \(\text{Y}^{3+}\) crystallize in a hexagonal structure unrelated to the perovskites. However, the metastable orthorhombic perovskite phase can be stabilized by high pressure synthesis or by changing the average ionic radius of the \(\text{R}\) site, i.e. by partial substitution of \(\text{Y}\) with \(\text{Gd}\) or \(\text{Ca}\) \cite{18}.

We synthesized the perovskite phase by substituting \(\text{Y}\) with \(\text{Ca}\). Due to the difference between the ionic radii of \(\text{Ca}\) and \(\text{Y}\) ions, the substitution is limited to the region \(0.2 \leq x \leq 1\). For this interval of \(\text{Ca}\) concentration, the value of the tolerance factor increases resulting in an increased stability of the perovskite structure. For a \(\text{Ca}\) concentration of \(x = 20\%\) we have grown a single crystal, and for the rest of the compositions \(30\%, 40\%, 50\%, 60\%,\) and \(70\%\) we have synthesized powder samples.

The single crystal analysis of the full data sets collected at 100 K and 295 K for the \(x = 20\%\) sample provided a full structure determination. At both temperatures, the data sets are consistent with the \(Pbmm\) symmetry and did not contain any extra reflections. Furthermore, the \(\omega - \chi\) scans performed with the CAD4 diffractometer did not reveal any twinning, excluding the possibility of a lower symmetry. Using the RT structure for orthorhombic \(\text{YMnO}_3\) (taken from the Ref. 7) as a starting point, we performed refinements in \(Pbmm\) symmetry. The very good quality data sets of the untwinned single crystal resulted in smooth refinements allowing us to accurately determine the position of the atoms. The refinement of the occupation of the \(4c\) position indicate an amount of \(20\%\) of \(\text{Ca}\) atoms incorporated in the structure. The results of the refinement at RT are presented in Appendix B, Table B.1.

No significant differences are observed in the refined positions of the atoms at 100 K and 293 K. The large difference of \(\approx 0.18\ \text{Å}\) between the in-plane long (\(l\)) and short (\(s\)) \(\text{Mn-O}_2\) bond lengths results in a JT distortion parameter of \(\Delta = 0.0025\) at both temperatures. The magnitude of the

\(\dagger\) The tolerance factor is defined as \(t = (r_{RE} + r_O)/[(r_{Mn} + r_O))/\sqrt{2}]\), where \(r_{RE}, r_{Mn}, r_O\) are the ionic radii of the \(\text{R}\), \(\text{Mn}\) and \(\text{O}\) ion, respectively. For an ideal perovskite structure, the ratio between the radii of the \(\text{R}\) ion and the \(\text{Mn}\) ion is such that the tolerance factor is equal to one.
rotation parameter is associated with the large deviation of the tilting angle Mn-O-Mn from 180°, \( i.e. 35.2° \).

For the \( x = 30\% \) sample we performed PXD experiments at RT on a Philips diffractometer using Cu-K\(_{\alpha 1}\) and Cu-K\(_{\alpha 2}\) radiation. The absence of the primary monochromator results in sufficiently large intensity to background ratio (\( \approx 10 \) times larger than the ratio obtained with the Bruker-D8 diffractometer) for reliable refinement of the fractional coordinates. The observed diffraction peaks can be indexed in \( Pbnm \) symmetry. We performed Rietveld analysis in this symmetry by refining the following parameters: scale factor, background coefficients, zero-point error, unit cell parameters, atoms fractional coordinates and Gaussian parameters for the peak shape. The results of the refinements are presented in Table B.1, Appendix B.

Figure 4.7: (a) Evolution of the JT distortion parameter \( \Delta \) and the tilting angle (inset) with the Ca concentration in \( Y_{1-x}Ca_xMnO_3 \) at RT. The values for the \( x = 0 \) and \( x = 0.5 \) samples are taken from Ref. 7 and Ref. 22, respectively. (b) \( Q_2, Q_3 \) distortions and Mn-O distances (inset) versus Ca concentration in \( Y_{1-x}Ca_xMnO_3 \) at RT.

In the \( Y_{1-x}Ca_xMnO_3 \) system, the JT Mn\(^{3+}\) ions are substituted by non-JT active Mn\(^{4+}\) ions. Therefore the JT parameter decreases with increasing the amount of Mn\(^{4+}\) ions and is completely suppressed for a 50% Ca concentration (as shown in Fig. 4.7(a)). Simultaneously, Y\(^{3+}\) ions are substituted by divalent Ca\(^{2+}\) ions with larger radius, resulting in a larger tolerance factor. Thus, the tilting angle decreases with the increasing of the average ionic radius of the R site as indicated in the inset of Fig. 4.7(a). In Fig. 4.7(b) we plot the two components, \( Q_2 = 2(l - s)/\sqrt{2} \) and \( Q_3 = 2(2m - l - s)/\sqrt{6} \) of the JT distortion parameter as a function of Ca concentration. We notice that with increasing Ca concentration the relative contribution of the Q3 component to JT distortion increases at the expense of the decrease of the Q2 component contribution. Due to the decrease of Q2 component more rapidly than the decrease of the Q3 component with increasing \( x \), the char-
acter of the distortion changes from predominant Q2 to predominant Q3. This change is reflected also in the ratio between the Mn-O_{1} and Mn-O_{2}-short distances which reverses above \( x = 0.2 \) as shown in the inset of Fig. 4.7(b). These results are in contrast with the the dominant contribution of the Q2 distortion independent of the size of the R ion in the parent members of the RMnO_{3} series (see Fig. 4.12(b)).

Figure 4.8: (a) and (b) Ionic radius dependence of \( (c/\sqrt{2})/a \) and \( b \) for \( Y_{1-x}Ca_xMnO_3 \) with \( x = 0, 0.2, 0.3, 0.5 \) and 0.7 at RT. The points corresponding to \( x = 0 \) and \( x = 0.5 \) are taken from Ref. 7 and Ref. 22. With square symbols we indicate the data at RT for RFeO_{3}, with \( R = Y, Tb, Gd, Sm \) and Nd (Ref. 24 and Ref. 25). The lines are guides for the eye.

In Fig. 4.8(a) and (b) we plot the \( (c/\sqrt{2})/a \) ratio and the \( b \) parameter dependence as a function of the average ionic radius of the R site at RT. In these plots we include also the points corresponding to non-JT distorted members of the RFeO_{3} series with similar R ionic radius, i.e. Y, Tb, Gd, Sm and Nd [25, 24]. We notice that contrary to RFeO_{3} series, \( a \) and \( c/\sqrt{2} \) do not change significantly for \( Y_{1-x}Ca_xMnO_3 \) series and thus the \( (c/\sqrt{2})/a < 1 \) is concentration independent, while the \( b \) parameter decreases strongly with increasing Ca doping. According to the criterion described in Section 4.2, the \( (c/\sqrt{2})/a \) ratio corresponds to the JT distorted O'-orthorhombic structure. However, from the RT refinements of the fractional coordinates of \( x = 0.5 \) sample [22] the JT parameter is suppressed at \( x = 0.5 \) (see Fig. 4.7). Furthermore, the \( b \) parameter drops dramatically with increasing the average ionic radius of the R site and saturates for \( x \approx 0.5 \) at a smaller value than the ones corresponding to RFeO_{3} series with an O-orthorhombic structure. This result can be attributed only to the decrease in JT parameter with the increase of the Ca concentration and gives further support to the absence of the JT distortion for \( x \geq 0.5 \). The \( (c/\sqrt{2})/a < 1 \) criterion was established for the JT distorted parent compounds of the RMnO_{3} series with dominant Q2 component. Based on the observed increasing of
the Q3 component with respect to the Q2 component with increasing Ca concentration, we conclude that the \((c/\sqrt{2})/a < 1\) criterion can not identify a cooperative JT distortion in \(Y_{1-x}Ca_xMnO_3\).

The high temperature behavior of \(x = 0.2, 0.3\) and 0.7 samples was studied by analyzing PXD performed on the Bruker-D8 diffractometer using Cu-K\(\alpha_1\) radiation. We performed Rietveld analysis in \(Pbnm\) space group by fixing the atoms positions at the values derived from the RT refinements and by refining the following parameters: scale factor, background coefficients, zero-point error, unit cell parameters and Gaussian parameters.

The temperature dependence of the unit cell parameters for the \(x = 0.2, 0.3\) and 0.7 samples are plotted in Fig. 4.9. We observe changes in the lattice parameters ratio from \(c/\sqrt{2} < a\) to \(c/\sqrt{2} > a\) at \(\approx 773\) K, \(\approx 625\) K and \(\approx 525\) K, for \(x = 0.2, 0.3\) and 0.7 respectively. The criterion introduced in Section 4.2 for JT distorted systems with dominant Q2 component, identifies such a change in the lattice parameters with a transition from an orbitally ordered O'-orthorhombic phase to an orbitally disordered O-orthorhombic phase. As discussed above, this criterion is not valid for \(Y_{1-x}Ca_xMnO_3\) with \(x > 0\), due to the increasing with \(x\) of the Q3 component contribution to the JT distortion. Furthermore, in contrast to NdMnO\(_3\), the change in the lattice parameters and in the molecular volume in \(Y_{1-x}Ca_xMnO_3\) is continuous at the point where \((c/\sqrt{2})/a\) ratio reverses and thus it does not possess the character of a phase transition. The RT refinements of the fractional coordinates indicating a critical Ca concentration of \(x \approx 0.5\) (see Fig. 4.7) gives further support that the reversing of the \((c/\sqrt{2})/a\) ratio at \(\approx 525\) K for \(x = 0.7\) can not be identified with an orbital order-disorder transition. For such large concentrations of Mn\(^{4+}\) ions, the temperature dependence of the cooperative tilting of the octahedra dominates the temperature dependence of the lattice parameters, while the role of the cooperative JT effect is less significant.

As indicated in Fig. 4.8, the unit cell parameters evolution with Ca doping at RT saturates at the critical Ca concentration, \(i.e.\) \(x \approx 0.5\). Thus, the temperature evolution of the lattice parameters for \(x = 0.7\) can be taken as a reference for the non-JT distorted phase. We notice that in the temperature interval we have performed the measurements, the difference between \(a, b\) and \(c/\sqrt{2}\) for \(x = 0.2\) and \(x = 0.3\) is large compared to the one for the non-JT distorted system with \(x = 0.7\). Based on this observation we conclude that for \(x = 0.2\) and \(x = 0.3\), the JT transition temperature was not reached within the temperature interval we have measured.

In Fig. 4.10 we show the temperature dependence of the electrical resistivity for the \(x = 0.2\) and \(x = 0.7\) samples. In the inset of Fig. 4.10 we plot the temperature derivative of the \(\ln(\rho)\) versus temperature for the \(x = 0.7\) sample showing the presence of two anomalies. The first anomaly around 115 K is attributed to the antiferromagnetic transition detected
Figure 4.9: Temperature dependence of the $Y_{1-x}Ca_xMnO_3$ ($x = 0.2; 0.3; 0.7$) unit cell parameters. The lines are guides for the eye.

by a neutron diffraction study [22], while the second one observed around 260 K corresponds to a charge order transition observed by the authors of Ref. 22 for $Y_{0.5}Ca_{0.5}MnO_3$. The resistivity measurement on $x = 0.2$ single crystal (along the $c$ axis) show a semiconductor behavior with an activation energy of 0.19 eV. The conductivity increases strongly with increasing the Ca concentration. However, even for a very large Ca concentration, i.e. $x = 0.7$, a pure metallic behavior is not observed. This contrasts to La$_{1-x}$Ca$_x$MnO$_3$, where the metallic state is obtained at the critical Ca con-
4.6 Effect of R size on Jahn-Teller distortion in $R_{1-x}Ca_xMnO_3$

In order to understand the high temperature behavior of the different members of the RMnO$_3$ series, we focus on the evolution with the size of the R ion of the two parameters of the perovskite structure: the rotation and JT parameter. The RT structure of RMnO$_3$ ($R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er$) was studied in great detail in part by Alonso et al. [7] and in part by Mori et al. [8]. A better insight in the individual contribution of the two parameters is obtained by comparing the RMnO$_3$ series with the non-JT series RFeO$_3$ [24].

In Fig. 4.11 we plot the rotation parameter for RMnO$_3$ [7, 8] and RFeO$_3$ [24, 25] as a function of the size of the R ion. For both systems, the rotation parameter defined as the deviation of the TM-O-TM tilting angle from 180° show a progressive increase with decreasing ionic radius. In Fig. 4.12(a) we plot the ionic radius dependence of the long, medium, short and average Mn-O bond lengths. As already discussed in the Section 4.2, the medium
bond length deviates from the average bond length, indicating that the JT distortion is not of a pure Q2 type, but also a contribution of the Q3 type of distortion is present. Again, we define the distortion of the octahedra by the parameter \( \Delta = (1/6) \sum_{n=1,6} [(d_n - <d>/ <d>)]^2 \). Fig. 4.12(b) show a small increase in \( \Delta \) from \( \text{LaMnO}_3 \) to \( \text{SmMnO}_3 \) followed by a plateau for the rest of the members of the \( \text{RMnO}_3 \) series. The deviation from this plateau in \( \text{YMnO}_3 \) and \( \text{ErMnO}_3 \) is suggested by the authors of Ref. 7 to be a result of the presence of significant amounts of \( \text{Mn}^{4+} \) ions due to the synthesis conditions (a \( \text{O}_2 \) flow was used to minimize the formation of the hexagonal phase). The ionic size dependence of the Q2 and Q3 components of the JT distortion are shown in the inset of Fig. 4.12(b). We notice that for all the members of the \( \text{RMnO}_3 \) series, the Q2 component is dominant and does not change significantly with the size of the R ion.

From the evolution of the rotation and JT parameters we can easily understand their effect on the R ionic size dependence of the lattice parameters in \( \text{RFeO}_3 [7, 8] \) and \( \text{RMnO}_3 [24, 25] \) shown in Fig. 4.13(a) and (b). For the \( \text{RFeO}_3 \) the effect of the pure rotation is to distort the parent cubic structure by deviating the \( (c/\sqrt{2})/a \) ratio from 1 resulting in the O-orthorhombic structure with \( b > c/\sqrt{2} > a \). Moreover, as expected for the decrease of the R ionic radius, this ratio shows a progressive increase with the rotation parameter. For the \( \text{RMnO}_3 \) series, the O’-orthorhombic structure with \( c/\sqrt{2} < a < b \) is obtained by superimposing the JT distortion on the O-orthorhombic structure. As shown in Fig. 4.11, the evolution
4.6. Effect of R size on Jahn-Teller distortion in $R_{1-x}Ca_xMnO_3$

![Diagram of Mn-O bond lengths and JT distortion parameter Δ with the R ionic radius at RT. The lines are guides for the eye. Inset: The Q2 and Q3 components of the JT distortion versus ionic size. For these plots, we used the data taken from Ref. 7 and Ref. 8.](image)

Figure 4.12: Evolution of the (a) Mn-O bond lengths and (b) JT distortion parameter $\Delta$ with the R ionic radius at RT. The lines are guides for the eye. Inset: The Q2 and Q3 components of the JT distortion versus ionic size. For these plots, we used the data taken from Ref. 7 and Ref. 8.

of the rotation parameter with R size is similar for the two series. Thus the change in the RMnO$_3$ lattice parameters in respect to RFeO$_3$ lattice parameters, i.e. $(c/\sqrt{2})/a$ ratio and $b$, is mainly affected by the magnitude of the JT parameter. The JT parameter for RMnO$_3$ series show an almost constant dependence on R (see Fig. 4.12(b)). Therefore the effect of the JT distortion in RMnO$_3$ series is mainly to shift the R dependence of the $(c/\sqrt{2})/a$ and $b$ curves obtained for RFeO$_3$ series, without much affecting their shape. As clearly results from the plots shown in Fig. 4.13(a) and (b), by going from RFeO$_3$ to RMnO$_3$, the effect of the JT distortion is twofold: to reverse the $(c/\sqrt{2})/a$ ratio and to increase significantly the $b$ parameter.
We will further discuss the effect of the R ionic size on the JT transition temperature ($T_{JT}$) and the critical Ca concentration (the concentration at which the JT distortion is suppressed) for the members of the RMnO$_3$ series. Our high temperature measurements on NdMnO$_3$ are in agreement with the high temperature measurements for different RMnO$_3$ [9, 10, 23]. This indicates that the orbital order-disorder transition occurs over a temperature interval $T^* < T < T_{JT}$ in which the two orthorhombic $Pbnm$ structures, i.e. O' and O coexist. From the plot in Fig. 4.14 (the data were taken from Ref. 2, 9, 10), we observe that similar to the rotation parameter (Fig. 4.11), the transition temperature $T_{JT}$ shows a progressive increase as the R ionic size decreases. In contrast, the JT parameter $\Delta$ (Fig. 4.12(b)) shows a very small variation with the R ionic radius. The difference between the lattice parameters, i.e. $a$, $b$ and $c/\sqrt{2}$ above $T_{JT}$, and thus the rotation above $T_{JT}$, increases with decreasing the ionic size radius. These results show that the rotation of the octahedra stabilizes the orbitally ordered state. However, the magnitude of the JT distortion is not significantly affected by the rotation parameter.

There are a few structural studies for different members of R$_{1-x}$Ca$_x$MnO$_3$ reporting the critical Ca concentration for which the orbital ordered state is completely suppressed. For La$_{1-x}$Ca$_x$MnO$_3$, a detailed structural study [3] indicate a critical Ca concentration of $\approx 21\%$. Furthermore, the unit cell lattice parameters evolution with $x$ in Eu$_{1-x}$Ca$_x$MnO$_3$ indicate a critical Ca concentration of 40% [26] (transition from O’- to O-orthorhombic structure). A more recent neutron diffraction study of Tb$_{1-x}$Ca$_x$MnO$_3$ [27] determined the fractional coordinates for the oxygen positions, allowing us to calculate the JT parameter as a function of $x$ and thus to determine the critical Ca concentration of $\approx 45\%$. We add to these results our own study on Y$_{1-x}$Ca$_x$MnO$_3$ which indicates the suppression of JT distortion.
for $x = 50\%$. Fig. 4.15(a) indicates the linear decrease of the critical Ca concentration with increasing the average ionic radius of the R site. The dependence of the JT parameter magnitude of $x$ for $R_{1-x}Ca_xMnO_3$ (with $R = \text{La, Tb and Y}$) is shown in Fig. 4.15(b). The parent compounds $RMnO_3$ do not show significant variations in the magnitude of JT distortion. However, the critical Ca concentration increases with increasing tilting angle of the $\text{MnO}_6$ octahedra. These results suggest that the rotation parameter is responsible for the stabilization of the orbital ordered state.

Complementary to these results, the JT transition temperature ($T_{JT}$) evolution with Ca concentration in different $R_{1-x}Ca_xMnO_3$ is of particular interest. The structural study on $\text{La}_{1-x}Ca_xMnO_3$ [3] indicates the decrease of the orbital order-disorder transition temperature with increasing Ca doping, and no JT distortion is observed for $x > 0.21$. For a system with a larger tilting angle, i.e. $\text{Pr}_{1-x}Ca_xMnO_3$, $T_{JT}$ was reported to decrease from 945 K for $x = 0$ to 330 K for $x = 0.3$ (for $x > 0.3$ the symmetry of the structure becomes tetragonal) [10]. For the large tilting angle compound $\text{YMnO}_3$ the transition temperature of $T_{JT} \approx 1600$ K is obtained by extrapolating the linear dependence of $T_{JT}$ on the ionic radius of the R depicted in Fig. 4.14. As derived from our own study on $\text{Y}_{1-x}Ca_xMnO_3$, the JT transition temperature for $x = 0.2$ and $x = 0.3$ was not reached within the temperature interval we have performed the high temperature measurements. The JT distortion is completely suppressed in $\text{Y}_{1-x}Ca_xMnO_3$ for a
Figure 4.15: (a) Critical Ca concentration to suppress JT distortions in $\text{RMnO}_3$ at RT versus the R ionic radius. (b) JT parameter dependence of the Ca concentration for $\text{RMnO}_3$ with $R = \text{La, Tb, Y at RT}$.

critical concentration of $x \approx 0.5$.

Figure 4.16: JT transition temperature dependence on Ca concentration for $\text{RMnO}_3$ with $R = \text{La (Ref. 3), Pr (Ref. 10) and Y}$.

In Fig. 4.16 we summarize these results to indicate the rotation effect on both temperature and Ca concentration. The data points for $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0.2$ and $x = 0.3$, represent the maximum temperatures we reached in our measurements. We mark these points with arrows to indicate that the JT transition temperatures are larger. Based on the increase of the transition temperature $T_{JT}$ and of the critical Ca concentration with the rotation, we conclude that the rotation is responsible for the stabilization of the cooperative JT distortion.
4.7 Conclusions

The high temperature structural investigation of NdMnO$_3$ indicate that the orbital order-disorder transition takes place within a temperature interval of $\approx 200$ K. In this temperature interval, the orbitally ordered O'-orthorhombic phase coexist with the orbitally disordered O-orthorhombic phase. The discontinuity in the temperature dependence of the lattice parameters and of the molecular volume at the transition between the two phases suggests a first order phase transition. Moreover, we found that for the measurements performed in air, the orbital order-disorder transition occurs 200 K lower than for the measurements performed in vacuum. Thus the measurements in air probe an oxidation phase NdMnO$_{3+\delta}$ which introduces non-JT active Mn$^{4+}$ ions.

The study of the doping effect on the cooperative JT distortion in Y$_{1-x}$Ca$_x$MnO$_3$ indicates the decrease of the JT parameter with increasing the amount of Mn$^{4+}$ ions. We found a critical Ca concentration for which the JT distortion is completely suppressed of $\approx 50\%$.

The effect of the R ionic size on the JT transition temperature ($T_{JT}$) and the critical Ca concentration for the members of the RMnO$_3$ is described as follows. The transition temperature $T_{JT}$ shows a progressive increase as the R ionic size decreases similarly to the rotation parameter, while the JT parameter shows a very small variation with the R ionic radius. The critical Ca concentration decreases linearly with increasing the average ionic radius of the R site (decreasing the tilting angle of the MnO$_6$ octahedra). Based on these observations, we conclude that the rotation is responsible for the stabilization of the cooperative JT distortion.
References


4.7. Conclusions


