Chapter 5

The hexagonal to orthorhombic structural phase transition

AMnO$_3$ compounds with $A = \text{a lanthanide with a larger ionic radius than Ho}^{3+}$ have the orthorhombic structural ground state. If $A = \text{Y or a lanthanide with a smaller radius than Dy}^{3+}$, a hexagonal structure is found. In this chapter, the focus is on the boundary between the two structural states. The relative stability of the two phases depends among others on synthesis and annealing temperature, average ionic radius of the A ion and the pressure. One part of the boundary region is the ionic radius gap between $r_{Y^{3+}}$ and $r_{Dy^{3+}}$. A crossing of the boundary is observed during high pressure synthesis of YMnO$_3$. The influence of high temperature annealing, which prefers the hexagonal phase, and synthesis route, which enables low temperature synthesis of the orthorhombic phase, is already known. Here, another parameter that partially controls the transition is introduced, the disorder or the variance of the ionic radii on the A site. The variance $\sigma^2$ is given by,

$$\sigma^2 = \sum_{i=1}^{n} x_i (r_i - \langle r_A \rangle)^2$$

(5.1)

It is shown that the transition in AMnO$_3$ from the orthorhombic perovskite phase to the hexagonal phase is promoted by inducing disorder on the A site. The ionic radius gap between the orthorhombic (o-DyMnO$_3$) and the hexagonal (h-YMnO$_3$) phases is widened for disordered, mixed yttrium-gadolinium manganite samples. At the cost of the orthorhombic phase a two phase region emerges. The phase separation exhibits very unusual thermodynamical behaviour.

We also show that high pressure synthesis favours the orthorhombic phase. YMnO$_3$ is formed in the orthorhombic phase at 15 kbar.

After a short introduction to both structures, including the effect of tolerance factor, the possibilities to create the unstable orthorhombic state are reviewed. Then the effect of cation disorder on the stable state of Y$_{1-x}$Gd$_x$MnO$_3$ is discussed. The last part of this chapter is dedicated to the experiments on high pressure synthesis of o-YMnO$_3$.  

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5.1 Introduction

In the search for new composition-properties relations $\text{ABO}_3$ compounds have attracted a lot of attention. The perovskite materials, $\text{ABO}_3$, have been researched extensively because this structure forms the basis for interesting physical properties such as high $T_c$ superconductivity [1] and colossal magnetoresistance [2–4]. Non-perovskite $\text{AMnO}_3$, with $\text{A} = \text{Y}, \text{Ho},...,\text{Lu}$, attracted renewed interest, due to their ferroelectric properties [5]. These hexagonal $\text{AMnO}_3$ [6, 7] have a basically different structure than most $\text{ABO}_3$ compounds, that are distorted perovskites. Although each crystal structure is very stable, only slight variations in the constituents or synthesising conditions are sufficient to transform the structure, with large changes in co-ordination, density and electronic properties.

The transition from the orthorhombic perovskite ($o$) to the hexagonal ($h$) phase is investigated by changing the average ionic radius of the A site and by high pressure synthesis. The effect of the ionic radius on the transition is studied by partially replacing Y by Gd ions in $\text{YMnO}_3$. The resulting phase diagram leads us to discuss the effect of disorder, in terms of the ionic radius variance, on the stability of the hexagonal and orthorhombic phases.

The basic building block of the perovskite is an oxygen octahedron with a transition metal, $B$, in its centre, see Fig. 2.1. The A ions, usually lanthanides or alkaline earth metal ions, occupy the holes between the octahedra, that form a 3D corner shared network. In this picture $B$ is sixfold and $A$ is twelvefold co-ordinated. Most perovskites have a distorted structure, derived from this building block. The distortions have various origins, including a ferroelectric transition for $B$ a $d^0$ transition metal ion like Ti$^{4+}$ [8]. The most common distortion however originates from the relatively small radius of the A ions compared with the holes between the octahedra. This results in a cooperative rotation [9] of the octahedra known as the GdFeO$_3$ rotation [10,11]. While the structure is interesting in its own right, it also has large effects on the physical properties. It is well documented that the physical properties strongly depend on the magnitude of the structural distortions. An overview for the manganites is given in Ref.’s [12, 13].

The magnitude of the GdFeO$_3$ rotation strongly depends on the tolerance factor $t$, see Eq. (2.1). The tolerance factor gives the relation between the radii of ions $A$, $B$ and $O$ in an ideal cubic perovskite. For $t = 1$ the size of the lanthanide is exactly right to compose the cubic perovskite system. For Mn$^{3+}$, $r_{\text{Mn}^{3+}} = 0.645$ Å and $r_{\text{O}^{2-}} = 1.42$ Å this yields a ionic radius $r_{A^{3+}} = 1.50$ Å, where the largest lanthanide, La, has a radius of 1.215 Å [14]. The corresponding tolerance factor, $t = 0.90$, indicates a large distortion for $\text{LaMnO}_3$. With increasing atomic number, the lanthanide radius decreases and thereby the distortion increases. For the manganites, the tolerance factor is conventionally regarded as the factor signalling the boundary between the hexagonal and orthorhombic structures. The orthorhombic perovskite phase is stable for $t > 0.855$, corresponding to $r_A \geq r_{\text{Dy}}$ [15]. For $t < 0.855$, $r_A \leq r_{\text{Ho}}$, the hexagonal phase prevails [6]. Yttrium, although not in the lanthanide series, behaves chemically identical and its radius falls between dysprosium and holmium. An overview on the ionic radii and tolerance factors of some relevant compounds is given in Table 5.1.
5.1. Introduction

The high temperature phase of the hexagonal AMnO\textsubscript{3} consists of eightfold co-ordinated A ions in bicapped antiprisms. Trigonal bipyramidal holes are formed between two layers of face-sharing antiprisms by the edges of the capping oxygen ions with the antiprisms. The capping oxygen ions of two adjacent layers are located on the same \textit{ab} plane. Half of the bipyramidal holes are occupied by Mn. The apical oxygen ions of the MnO\textsubscript{5} bipyramid are also the oxygen ions that make up the antiprism. The two polyhedra are sketched in Fig. 5.1, where the shared edge is shown. The Mn--O\textsubscript{ap} distance is thus equal to the distance between the antiprism oxygen layer and the capping oxygen layer. The steric hindrance of the Mn restricts this layer separation and therefore increases the A--O\textsubscript{ap} bond length. Thus, the eightfold co-ordination is not uniform. The two apical oxygen ions have slightly larger bond lengths. Furthermore, the structure is unstable against a ferroelectric distortion at lower temperatures. The apical oxygen ions move in such a way that one bond becomes ‘normally’ short, while the other becomes about 1 Å larger.

![Sketch view of the local environment, showing AO\textsubscript{7}, left side, and MnO\textsubscript{5}, right side. Atoms marked with "*" and with "x" are identical, the thick line indicates the shared edge.](image)

Although the hexagonal phase of YMnO\textsubscript{3} at ambient conditions is the thermodynamically stable phase, there are several ways to obtain orthorhombic YMnO\textsubscript{3}. Already in

<table>
<thead>
<tr>
<th>A\textsuperscript{3+} ion</th>
<th>ionic radius (Å)</th>
<th>tolerance factor (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1.215</td>
<td>0.902</td>
</tr>
<tr>
<td>Gd</td>
<td>1.109</td>
<td>0.866</td>
</tr>
<tr>
<td>Dy</td>
<td>1.083</td>
<td>0.857</td>
</tr>
<tr>
<td>Y</td>
<td>1.075</td>
<td>0.854</td>
</tr>
<tr>
<td>Lu</td>
<td>1.032</td>
<td>0.840</td>
</tr>
</tbody>
</table>

Table 5.1: Ionic radii and tolerance factors for relevant AMnO\textsubscript{3} compounds.
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<table>
<thead>
<tr>
<th>A$^{3+}$ ion</th>
<th>Pressure (kbar)</th>
<th>Temperature ($^\circ$C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>34</td>
<td>650</td>
<td>Waintal et al. [19]</td>
</tr>
<tr>
<td>Y</td>
<td>45</td>
<td>900</td>
<td>Waintal et al. [19]</td>
</tr>
<tr>
<td>Y</td>
<td>35</td>
<td>1000</td>
<td>Wood et al. [20]</td>
</tr>
<tr>
<td>Ho</td>
<td>45</td>
<td>950</td>
<td>Waintal et al. [19, 21]</td>
</tr>
<tr>
<td>Ho</td>
<td>35</td>
<td>1000</td>
<td>Wood et al. [20]</td>
</tr>
<tr>
<td>Er</td>
<td>42</td>
<td>675</td>
<td>Waintal et al. [19, 21]</td>
</tr>
<tr>
<td>Tm</td>
<td>42</td>
<td>780</td>
<td>Waintal et al. [19, 21]</td>
</tr>
<tr>
<td>Yb</td>
<td>42</td>
<td>700</td>
<td>Waintal et al. [19, 21]</td>
</tr>
<tr>
<td>Yb</td>
<td>40</td>
<td>1000</td>
<td>Wood et al. [20]</td>
</tr>
<tr>
<td>Lu</td>
<td>42</td>
<td>750</td>
<td>Waintal et al. [19, 21]</td>
</tr>
</tbody>
</table>

Table 5.2: A literature overview of high pressure experiment.

the 1960’s Yakel et al. reported “In the case of YMnO$_3$ two distinct and separable crystal habits were observed, one plate-like, (our hexagonal crystals are platelets) the other more prismatic.” [6]. Using thin film growth, an appropriate substrate will force the coherent growth of the orthorhombic phase [16].

Another way to obtain o-YMnO$_3$ is to reduce the reaction temperature. The thermally promoted diffusion of the cations is replaced by dissolving the metal oxides, for instance in citric acid. A sol-gel pyrolysis of the organic precursors yields a “green” product, which can be sintered at relatively low temperatures. Depending on the sintering temperature or the oxygen pressure, the orthorhombic phase is obtained in larger or smaller fractions. A high temperature anneal of either the “green” product or the o-YMnO$_3$ always returns the hexagonal phase [17].

Waintal et al. showed that high pressure synthesis can produce the distorted perovskite phase for HoMnO$_3$ [18]. A more elaborate study by Waintal and Chenavas gave critical transition temperatures and pressures for the whole lanthanide series. Synthesis of YMnO$_3$ will yield the orthorhombic phase at 34 kbar and 923 K [19]. High pressure synthesis favours the orthorhombic phase, because it has a higher density. In Table 5.2 an overview of high pressure experiments that yielded the orthorhombic phase is given.

5.2 Experimental

Polycrystalline ceramic samples of AMnO$_3$, where A is a mixture of Y and Gd, have been synthesised using regular solid state synthesis at ambient pressure. Starting materials were Y$_2$O$_3$, Gd$_2$O$_3$ and MnO$_2$. Stoichiometric amounts corresponding to formulae which range from pure YMnO$_3$ to pure GdMnO$_3$ were weighted and wet-mixed using acetone as liquid medium. The pressed pellets were sintered for 24 hours at 1250°C and for 24 hours at 1400°C.

High pressure experiments were carried out both on the mixture of oxides and on as-
5.3. High pressure synthesis

We applied high pressure and high temperature to convert or synthesise some of the conventionally hexagonal samples in the orthorhombic state. Pressure generally stabilises the most dense phase. The density of the orthorhombic and hexagonal phase are roughly $5.6 \times 10^3$ and $5.1 \times 10^3$ kg m$^{-3}$, respectively. Therefore, pressure favours the orthorhombic structure. First, we consider samples with $\sigma^2 = 0$. YMnO$_3$ is still hexagonal at 5 kbar, but the orthorhombic phase is found using a pressure of 15 kbar. The pressure-ionic radius phase diagram is shown in Fig. 5.2. The necessary pressure for the h-o transition, less than 15 kbar, is much less than the 34 kbar, reported previously in the literature [19]. The h-o transition phase line has been sketched in Fig. 5.2 by using midpoints. Extrapolating the pressure dependence of the h-o transition yields a critical pressure of $\lesssim 27$ kbar for HoMnO$_3$. The error bar on this value, $\sim 10$ kbar, is large because of the sparse data points.

We also carried out high pressure experiments on the Y$_{1-x}$Gd$_x$MnO$_3$ compounds. The necessary pressure to induce the orthorhombic phase from the phase mixture decreased with increasing $\langle r_A \rangle$. The $x = 0.06$ sample, which is hexagonal at ambient pressure, yields the orthorhombic phase after high pressure synthesis at 10 kbar. The $x = 0.19$ and $x = 0.25$ samples showed the two phases after standard solid synthesis. These samples turned orthorhombic after high pressure synthesis at 10 kbar and 5 kbar respectively. The $x = 0.5$ sample is already orthorhombic at ambient pressure synthesis.
pressure (kbars)

average radius $\langle r_A \rangle$ (Å)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\langle r_A \rangle$ (Å)</th>
<th>$t$</th>
<th>$\sigma^2$ ($10^{-6}$Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.075</td>
<td>0.854</td>
<td>0</td>
</tr>
<tr>
<td>0.06</td>
<td>1.077</td>
<td>0.855</td>
<td>68</td>
</tr>
<tr>
<td>0.19</td>
<td>1.081</td>
<td>0.857</td>
<td>176</td>
</tr>
<tr>
<td>0.25</td>
<td>1.084</td>
<td>0.857</td>
<td>217</td>
</tr>
<tr>
<td>0.31</td>
<td>1.086</td>
<td>0.858</td>
<td>248</td>
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<tr>
<td>0.38</td>
<td>1.088</td>
<td>0.859</td>
<td>271</td>
</tr>
<tr>
<td>0.5</td>
<td>1.092</td>
<td>0.860</td>
<td>289</td>
</tr>
<tr>
<td>1</td>
<td>1.109</td>
<td>0.866</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.3: Ionic radii, tolerance factors and variance of the studied $Y_{1-x}Gd_xMnO_3$ samples.

By changing the value of $x$ we substitute $Y$ by Gd, whereby $\langle r_A \rangle$ increases linearly. The tolerance factor of orthorhombic DyMnO$_3$ is equal to that of $Y_{1-x}Gd_xMnO_3$, with
x = 0.23. Thus for x ≥ 0.23 we expect to observe the orthorhombic phase. For smaller x and t the hexagonal phase is expected. For x = 0 and x = 0.06 we indeed found the hexagonal structure. However, for 0.19 ≤ x ≤ 0.38 we do not observe a sharp transition to the orthorhombic structure, but a mixture of the hexagonal and orthorhombic phases is observed. Only for x = 0.5 an (almost) pure orthorhombic compound is found. The anomalous behaviour of the mixed Y,Gd samples is best illustrated by focusing on the sample with x = 0.25, which has an almost identical tolerance factor as DyMnO₃. Where the latter sample is orthorhombic, the former segregates into two phases. The only difference between the two compounds is that one is undoped, σ² = 0 and the other has a mixed lanthanide composition, σ² > 0.

![Figure 5.3: Phase diagram of Y₁₋ₓGdₓMnO₃ as a function of r_A and σ². Diamonds, triangles and squares indicate hexagonal, mixed and orthorhombic phases. The drawn lines are estimates of the phase boundaries as explained in the text.](image)

The lattice parameters and the relative amounts of orthorhombic and hexagonal fractions are determined by Rietveld refinement of the powder diffraction data. The lattice parameter a is plotted in Fig. 5.4. The lattice parameter c is independent of ⟨r_A⟩ as shown in Table 4.1 and discussed in Section 7.2.2. We can rule out segregation of Y and Gd, since the continuous increase in the lattice parameter a of the hexagonal phase with increasing Gd concentration indicates perfect mixing of the A ions. A linear increase in a with ⟨r_A⟩ is also observed for the single A cation h-AMnO₃ series [6, 7, 28, 29]. Fig. 5.5 shows that the fraction of the orthorhombic phase increases linearly with the Gd concentration. This allows us to apply the lever rule on the h-o transition

\[
\frac{x - x_{\text{hexa}}}{x - x_{\text{ortho}}} = \frac{y_{\text{ortho}}}{y_{\text{hexa}}}
\]  

(5.2)
Figure 5.4: Lattice parameter $a$ of the hexagonal phase as a function of the Gd content $x$.

where $x_{\text{hexa}}$ and $x_{\text{ortho}}$ are the boundary values for the respective phases and $y_{\text{ortho}}/y_{\text{hexa}}$ the ratio of the two fractions. From the observed ratios $y_{\text{ortho}}/y_{\text{hexa}}$ as a function of $x$, the boundary values are derived. The boundary values derived from all five mixed phase samples are plotted in Fig. 5.3 as inverted triangles.

We construct a preliminary phase diagram by assuming that the h-o transition at $\sigma^2 = 0$ occurs halfway between hexagonal YMnO$_3$ and orthorhombic DyMnO$_3$. The phase boundaries are drawn in Fig. 5.3 as straight lines through the two calculated boundary values and the assumed $\sigma^2 = 0$ midpoint. This phase diagram can be described as follows. The phase line associated with the upper $t$ limit of the pure hexagonal phase does not depend on the variance. Slightly increasing $\sigma^2$ and $t$ results in the appearance of a two phase region, consisting of both the hexagonal and the orthorhombic phase. With increasing tolerance factor, the fraction of the orthorhombic phase increases until the lower boundary limit for the orthorhombic phase is crossed. This limit strongly depends on $\sigma^2$. The lower limit for the orthorhombic phase increases from $\langle r_A \rangle = 1.078$ Å at $\sigma^2 = 0$ to $\langle r_A \rangle = 1.093$ Å at $\sigma^2 = \sigma^2_{\text{max}}$. Note that $\langle r_A \rangle = 1.093$ Å corresponds with the ionic radius of terbium, the second smallest lanthanide to form the perovskite structure.

We have shown the dependence of the h-o transition on the average radius $\langle r_A \rangle$ and $\sigma^2$. In the next section, the effect of high pressure experiments on the h-o transition will be discussed.

5.5 Discussion of the disorder

We note the following observations of the two-phase region:
5.5. Discussion of the disorder

Figure 5.5: Relative amounts of hexagonal, triangles, and orthorhombic, squares, fractions as a function of the Gd content $x$. An open square is plotted for DyMnO$_3$ at the corresponding value of the tolerance factor.

1. The phase mixture is only observed after ambient pressure synthesis for samples with $\sigma^2 \neq 0$.

2. We do not observe the mixed phase for any of the experiments at high pressure ($\geq 5$ kbar). We cannot exclude the presence of the mixed phase at lower pressures, but our experimental set-up is not well-suited for those pressures.

3. The lattice parameters of both phases in the two phase region indicate no segregation into Y-rich and Gd-rich phases, see Fig. 5.4, which is unconventional.

4. Literature reports that synthesis via organic precursors can result in a mixture of hexagonal and orthorhombic phases for AMnO$_3$, $\sigma^2 = 0$, compounds [17].

These observations lead to the following conclusions. For $\sigma^2 = 0$ compounds either the hexagonal or the orthorhombic structure is stable. Whereas low temperature synthesis may yield mixed phase samples, a high temperature annealing will convert the unstable phase and realises a pure single phased sample. Either the hexagonal or the orthorhombic phase will be stable depending on the tolerance factor. However for $\sigma^2 \neq 0$ mixed phase samples can be obtained for a broad range of tolerance factors. Even a high temperature annealing retains the phase segregated state. Surprisingly, the phase segregation is not accompanied by the existence of two limiting compositions, e.g. $Y_{1-x}Gd_xMnO_3$ with $x = 0.1$ and $x = 0.5$. The continuous increase of the lattice parameters of both the hexagonal and the orthorhombic phase throughout the two phase region indicates that the composition of the hexagonal and the orthorhombic state are the same. We have no explanation for this unconventional form of phase segregation.
5.6 Conclusions

We have constructed phase diagrams for the hexagonal and orthorhombic phases of AMnO$_3$, including the effects of average ionic radius, hydrostatic pressure and variance. For compounds with $\sigma^2 \neq 0$ a phase separation in the orthorhombic phase and the hexagonal phase is found. The mixed region exists only at low pressures. We have shown that, at ambient pressure, this region expands towards higher values of the average radius with increasing variance. The upper limit for the pure hexagonal phase is not affected by an increase in the variance. We speculate that disorder, introduced by a large variance or soft chemical synthesis routes, allows the occurrence of the phase separation in the absence of other driving forces. Suppressing the disorder by applying external pressure or annealing at high temperatures prevents the existence of the phase separation. Pressure favours the denser, orthorhombic phase, whereas thermal annealing promotes the hexagonal phase.

references

5.6. Conclusions

[22] Quickpress 3.0 piston cylinder apparatus, operations manual (Depths of the Earth Company, 738 S. Perry lane, Tempe, Az, USA).
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