Chapter 2

Hexagonal rare-earth manganites, HoMnO$_3$

The hexagonal rare-earth manganites with a chemical composition REMnO$_3$ (RE = trivalent rare-earth cation, Ho-Lu, Y) possess a specific nature arising from the strong interplay between the $3d$ electrons of the transition metal Mn^{3+} and the $4f$ electrons of the rare earth ion RE^{3+}. REMnO$_3$ both the hexagonal and the perovskite-type structure have attracted interest so far because of their two outstanding properties, i.e. colossal magnetoresistance (CMR) and multiferroicity.

The CMR effect is a phenomenon of spin-dependent electron transport that leads to conductivity changes by several orders of magnitude at the ferromagnetic Curie temperature. This has been the subject of intense research in (doped and undoped) REMnO$_3$ manganites which have a distorted perovskite or orthorhombic structure [von Helmolt 93].

On the other hand, multiferroic properties, or the combination of ferroelectric and magnetic ordering was observed in REMnO$_3$ (RE=Eu-Lu, Y, Bi). The mutual interference and the possible correlation between the order parameters are of an academic as well as an application research interest.

In this chapter, the various physical properties of the hexagonal rare-earth manganites will be discussed. Among the REMnO$_3$ series, HoMnO$_3$, which turned out to be multiferroic showing strong magnetoelectric coupling [Lottermoser 04b] with large polarization (P = 5.6 μC/cm^2) and effective magnetic moment (μ_{eff} = 11.4 μ_B) [Fujimura 96, Lorenz 05], will be mainly addressed.

2.1 Crystal structure

2.1.1 Influence of RE^{3+} radius on crystal structure

The rare-earth manganites, REMnO$_3$, crystallize in the hexagonal or orthorhombic structure depending on the radius of the rare-earth ion RE^{3+}. The large ionic radius rare-earth ions (La and Ce-Dy) crystallize in an orthorhombic (distorted perovskite) structure. In contrast, the small ionic radius rare-earth ions (Ho-Lu and Y, Sc) crystallize in a hexagonal structure [Yakel 63]. This is because the decreasing size of the rare-earth series cations with increasing atomic number would decrease the stability of an orthorhombic lattice.

This tendency was shown quantitatively by the calculation of the thermodynamic free energy for crystallization by Graboy *et al.* [Graboy 03]. As it is shown in Fig.2.1, the Ho^{3+} ion is located at the border of the hexagonal and the orthorhombic structures. The potential energy difference between hexagonal and orthorhombic structure for Ho^{3+} is very small. This indicates that HoMnO$_3$ can also crystallize in the orthorhombic structure as a metastable state [Brinks 01, Lorenz 04b]. The
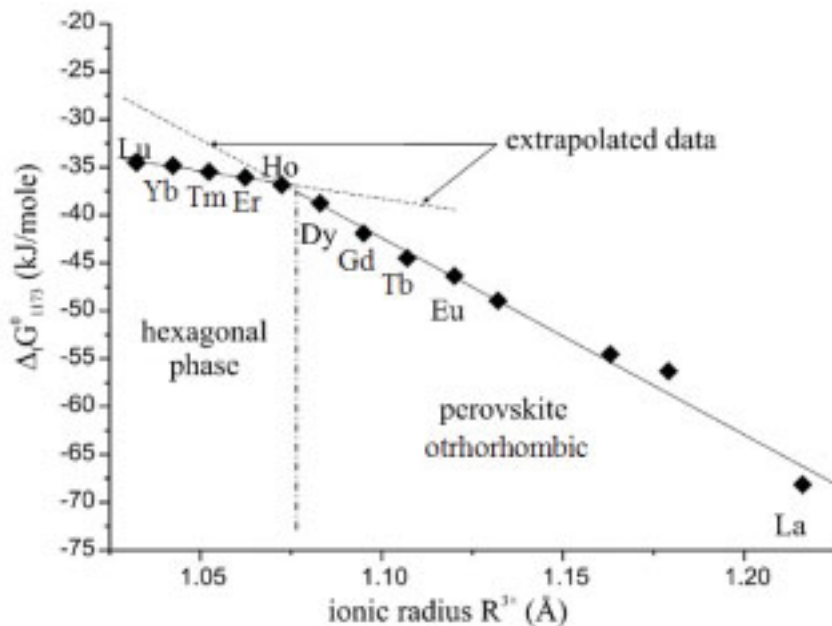

Figure 2.1: Free energy of bulk REMnO$_3$ formation from RE$_2$O$_3$ and Mn$_2$O$_3$ at 1173 K. The change of crystal structure depending on the radius of the RE^{3+} ion is quantitatively shown [Graboy 03].

scope of this dissertation is confined to the thermodynamically stable hexagonal structure.

2.1.2 Hexagonal HoMnO$_3$

Hexagonal HoMnO$_3$[†] is ferroelectric with a high ferroelectric Curie temperature $T_{CE} = 875$ K [Fujimura 96]. In the ferroelectric state, HoMnO$_3$ has a space group $P6_3cm$. Figure 2.2 shows the crystal structure of HoMnO$_3$ in the ferroelectric state.

In this structure, one Mn atom and five adjacent oxygen atoms form a MnO$_5$ trigonal bipyramid. Each Mn atom occupies the center of a triangular bipyramid whose vertices are oxygen atoms. The rare-earth ions are located in layers between the bipyramid sheets. The crystal structure is an alternative stacking of MnO$_5$ and rare-earth atom layers along the hexagonal c-axis.

The MnO$_5$ bipyramids share their corners with neighboring bipyramids to form a triangular lattice in the basal ab plane, where, each oxygen ion links three Mn ions, and each Mn ion is surrounded by three oxygens (Fig.2.2 (left)). In this triangular
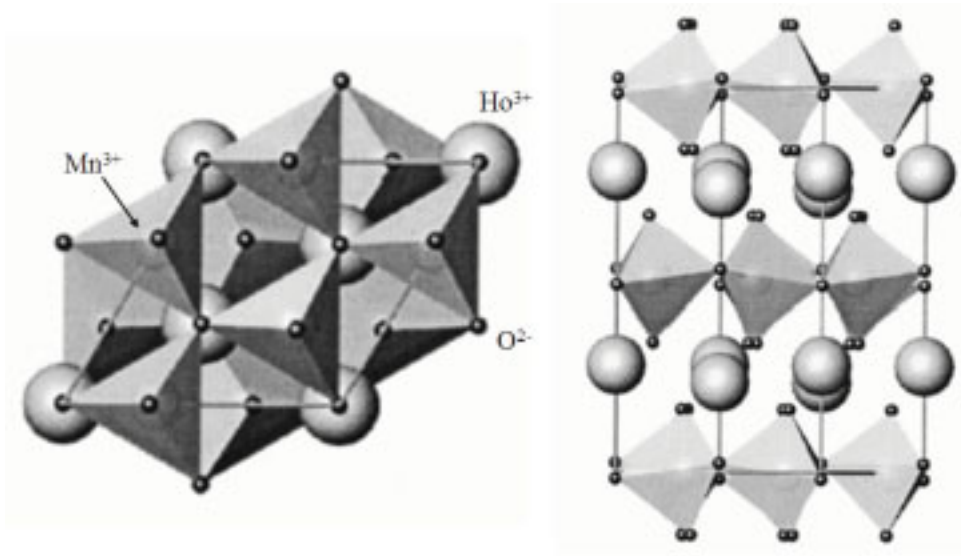

Figure 2.2: Hexagonal structure of HoMnO$_3$ in the ferroelectric state [Lonkai 03]. (left) Top view (ab plane), (right) side view (along c-axis). The big spheres indicate Ho^{3+}, the small spheres O^{2-}. Mn^{3+} lies in the middle of the trigonal bipyramids.

[†]In this dissertation from now on, if the term 'HoMnO$_3$' stands alone, it basically indicates hexagonal HoMnO$_3$.

arrangement the Mn atoms constitute a frustrated spin ordering (see §2.2.1). The Mn sublattice has a six-fold symmetry as a whole. This is because one Mn layer (at $z = 0$) forms one triangle and the next Mn layer (at $z = c/2$) forms a triangle rotated by 60°.

2.1.3 Ferroelectricity in hexagonal REMnO$_3$

The ferroelectricity in hexagonal REMnO$_3$ was firstly discovered by Bertaut *et al.* in 1963 [Bertaut 63a]. Since then, precise structural investigations have been employed to find the origin of ferroelectricity in hexagonal rare-earth manganites [Yakel 63, Van Aken 01, Van Aken 04, Nénert 07]. As a result, it is known that ferroelectricity is geometrically driven by the displacement between RE^{3+} and O^{2-} as a result of a structural phase transition.

Hexagonal REMnO$_3$ undergoes a structural phase transition from a high tem-

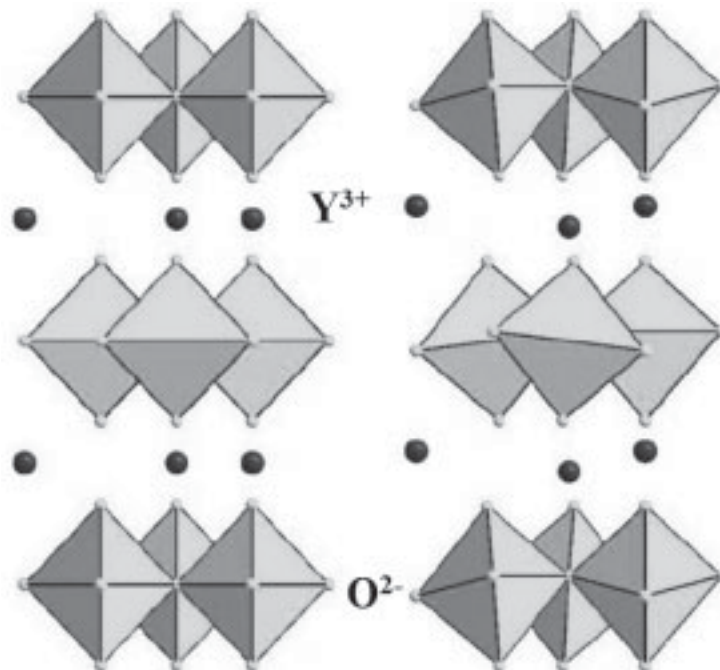Figure 2.3: High-temperature centrosymmetric (left) and low-temperature ferroelectric structure (right) of YMnO$_3$. At low temperatures, the oxygen-polyhedra are rotated collectively, accompanying the displacement of Y^{3+} along the c-axis. The displacement of Y^{3+} ions relative to the oxygen anions produces an electric dipole moment [Ederer 05].

perature paraelectric phase (space group $P6_3/mmc$) to the low temperature ferro-electric phase (space group $P6_3cm$) as the temperature decreases. Figure 2.3 shows the structures of these two states in YMnO$_3$. YMnO$_3$ may serve as representative of all hexagonal rare-earth manganite systems, especially for HoMnO$_3$ with its similar size of rare-earth ion and lattice parameters.

In the paraelectric phase (above the ferroelectric Curie temperature, T_{CE}), all ions are confined to planes parallel to the *ab* plane. This arrangement of atoms makes the structure centrosymmetric. Below the ferroelectric transition temperature, however, two major atomic displacements take place in the crystal structure from the centrosymmetric $P6_3/mmc$ to the ferroelectric $P6_3cm$. The first change is the collective rotation of the MnO$_5$ bipyramids. The second change is the vertical shift of the rare-earth ions away from the high-temperature mirror plane [Lonkai 04, Van Aken 04]. In this distortion, the Mn ions remain very close to the center of the oxygen bipyramids, giving no significant contributions to the polarization. The displacement of the rare-earth ions along the *c*-axis plays a crucial role for inducing ferroelectricity. The polar direction, therefore, is parallel to the *c*-axis. The value of the spontaneous polarization of hexagonal HoMnO$_3$ is known to be 5.6 μC/cm^2 [Fujimura 96].

2.2 Magnetic structure

The magnetic structure of REMnO$_3$ was first investigated in the middle of the 1960's by Bertaut *et al.* [Bertaut 63b] and Koehler *et al.* [Koehler 64] by neutron diffraction experiments. Before these experiments, a theoretical work of the magnetic structure of the nickel-arsenide type crystals was published [Hirone 57]. Because NiAs has a compatible structure with REMnO$_3$, i.e. a hexagonal structure with six-fold sublattices, this work was a guideline for early magnetic structure studies. Hirone *et al.* suggested four possible spin orders in this structure: ferromagnetic, uniaxial antiferromagnetic and two triangular antiferromagnetic orders. Bertaut *et al.* and Koehler *et al.* argued that, among these four spin orders, only the two triangular antiferromagnetic ones could be possible in REMnO$_3$ according to neutron diffraction experiments (Fig.2.4). These two triangular arrangements were named model α and β depending on how the Mn layers at $z = 0$ and $z = c/2$ are coupled to each other.

As shown in Fig.2.4, model α has a parallel arrangement between the $z = 0$ and $z = c/2$ layers, whereas model β has an antiparallel arrangement. The magnetic

space groups are determined by the combination of the relative spin directions in the two layers. The corresponding magnetic space groups of model α are $P\underline{6}_3\underline{c}m$ and $P\underline{6}_3c\underline{m}$. On the other hand, $P6_3cm$ and $P6_3\underline{c}\underline{m}$ belong to model β.

Even though the magnetic structure has been predicted theoretically and the triangular structure could be confirmed by neutron diffraction, the precise magnetic structure was controversial. Because it could not be distinguished easily by neutron diffraction whether the coupling between the $z = 0$ and $z = c/2$ layers is ferromagnetic or antiferromagnetic. Furthermore, it was not possible to properly discriminate the directions of the magnetic moments of the two triangular arrangements, e.g. the magnetic space groups $P6_3cm$ and $P\underline{6}_3c\underline{m}$.

In recent years, magnetic structure determination became possible by new techniques of statistical analysis of neutron powder diffraction data [Muñoz 01, Lonkai 02, Vajk 05] or by the non-linear optical method of second harmonic generation (SHG)
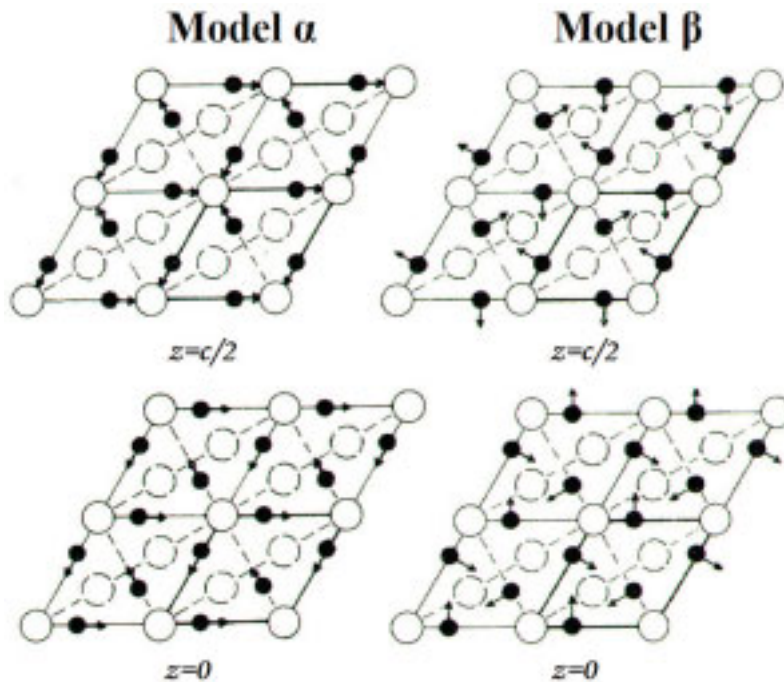

Figure 2.4: Two possible spin models named model α and β by Bertaut *et al.* according to Mn spin ordering. Model α has a parallel spin order in adjacent planes ($z = 0$ and $c/2$) and model β has an antiparallel spin order. Open and solid circles indicate rare-earth ions and Mn ions, respectively. Arrows mean spin order [Bertaut 63b].