

Compound Systems in Nonextensive Statistical Mechanics and Manganites

Compound Systems in Nonextensive Statistical Mechanics and Manganites

By

Felipe Américo Reyes Navarro

**Cambridge
Scholars
Publishing**



Compound Systems in Nonextensive Statistical Mechanics
and Manganites

By Felipe Américo Reyes Navarro

This book first published 2022

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Copyright © 2022 by Felipe Américo Reyes Navarro

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN (10): 1-5275-8445-3

ISBN (13): 978-1-5275-8445-7

To
my parents Américo and Julia,
and my brother Gustavo

Everything is theoretically impossible, until it is done.

—Robert A. Heinlein

If I have seen further, it is by standing on the shoulders of Giants.

—Isaac Newton

Impossible only means that you have not found the solution yet.

—Anonymous

The measure of intelligence is the ability to change.

—Albert Einstein

The snake which cannot cast its skin has to die. As well the minds which are prevented from changing their opinions; they cease to be mind.

—Friedrich Nietzsche

All I need is a sheet of paper and something to write with, and then I can turn the world upside down.

—Stephen Hawking

TABLE OF CONTENTS

List of Figures.....	xi
List of Tables.....	xii
Acronyms	xiii
Foreword	xiv
Preface	xv
Introduction	1
Part I Manganites	
Chapter One	4
Introduction to the Physics of Manganites	
A Brief Historical Outlook.....	4
General Formula	5
Crystal Structure	5
Pyrochlore Manganites.....	7
Electronic Structure	8
Main Theories Seeking to Unravel the Physics of Manganites.....	8
Phase Separation Scenario	12
Charge-Ordering Phase Transition.....	14
Orbital Ordering.....	15
The $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ Series	15
A Summary of Some Models for Manganites From First Principles..	16
Nanostructured Manganites	17
Potential Technological Applications	18

Part II Nonextensive Statistical Mechanics

Chapter Two	22
Nonextensive Statistical Mechanics	
Historical Events	22
Entropies Successfully Applied in Different Areas of Science	28
Thermodynamic Entropy	28
Boltzmann Entropy	28
Shannon Entropy	29
Quantum Group Entropy	29
κ -Entropy	30
Superstatistics	30
Basic Concepts of the Third Version of Nonextensive Statistical Mechanics	31
Tsallis Entropy	32
Demonstrating How to Obtain Tsallis Entropy Without Postulating It	33
Demonstrating that the q -Exponential and q -Logarithm are Inverse Functions	36
The Connection Between Renyi Entropy and Tsallis Entropy ..	37
Pseudo-additivity for Tsallis Entropy	38
Definition of Temperature	39
Nonextensive Quantum Mean Values	40
Escort Distributions	42
Escort Entropy	43
Entropy Optimization: Maximization and Minimization	44
Some Demonstrations by Using the Maximum Entropy Method	45
Boltzmann-Gibbs-Shannon Entropy Maximization	45
Boltzmann-Gibbs-Shannon Entropy Maximization for a Canonical ensemble	45
Boltzmann-Gibbs-Shannon Entropy Maximization for a Grandcanonical Ensemble	46
Tsallis Entropy Maximization in the First Version of Nonextensive Statistical Mechanics	48
Tsallis Entropy Maximization in the Second Version of Nonextensive Statistical Mechanics	50
Tsallis Entropy Maximization in the Third Version of Nonextensive Statistical Mechanics	51
Demonstrating What the Lagrange Multipliers Are (in the BGS Entropy Maximization)	54

Demonstrating What the Lagrange Multiplier α Is (for a Canonical Ensemble)	55
Demonstrating What the Lagrange Multiplier β Is (for a Canonical Ensemble)	55
Demonstrating What the Lagrange Multiplier α Is (for a Grandcanonical Ensemble)	57
Demonstrating What the Lagrange Multipliers β And γ Are (for a Grandcanonical Ensemble)	57
Demonstrating How to Obtain Boltzmann Entropy from Boltzmann-Gibbs-Shannon Entropy	59
Demonstrations of Several Properties of the q -Exponential Function ...	60
Finding Out a Formula for the q -Exponential Function of the Sum of Two Functions	60
Finding Out a Formula for the q -Exponential Function of the Sum of Three Functions	61
Demonstrating a Formula for the q -Exponential of the Sum of n Functions	62
Finding Out a Formula for the Product of Two q -Exponentials.....	64
Finding Out a Formula for the Product of Three q -Exponentials.....	65
Finding Out a Formula for the q -Exponential of the Difference of Two Functions	66
Finding Out a Formula for the Division of Two q -Exponentials ..	67
Chapter Three	69
An Alternative Method to Calculate Mean Values of Compound Systems	
A Formal Derivation from the Full Hilbert Space Toward the Hilbert Subspaces.....	69
On the Exemplifying Magnetic Model to Be Utilized	73
Mean Values of a Two Spin- $\frac{1}{2}$ System (Third Version of Nonextensive Statistical Mechanics).....	74
Applying an Alternative Method to Calculate Mean Values of Compound Systems.....	76
Additional Calculation for a System $A + B$ With Interaction	77
Some Detailed Calculations	79
Analytical Calculus for $q = 2$	80
The Escort Distributions of Compound Systems in Nonextensive Statistical Mechanics	82

Part III Applications

Chapter Four	86
Application of the Matrices E : a Model for $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0.30-0.50$	
Evidence for Nonextensive Magnetism in Manganites.....	86
Experimental Curves.....	87
Quasi-probability Distributions.....	91
Nonextensive Quasi-probability Distributions	92
A Model for $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.30-0.50$) Under Weak Magnetic Fields	93
Preliminary Formulae.....	93
The Model	94
 Chapter Five	 99
In Summary	
 Appendix A	 100
Topics on Magnetism	
 Appendix B.....	 104
Demonstration of Several Properties of the q -Logarithm Function	
 Appendix C.....	 111
Demonstration of Several Properties of the q -Operations and q -Gaussian	
 Bibliography.....	 135
 Index.....	 137

LIST OF FIGURES

- 1.1. Cubic perovskite structure.
- 1.2. Energy levels of the Mn^{3+} ion.
- 1.3. Major theories for manganites.

- 3.1. For mean values of a system $A + B$, a layout showing the summarized formal derivation from the full Hilbert space to the Hilbert subspaces.
- 3.2. Statistical independence in the third version of nonextensive statistical mechanics.
- 3.3. For spins $S_A = 2$ and $S_B = 3/2$, magnetization vs. temperature ($M_{A(B)}$ vs. T) by using the third version of nonextensive statistical mechanics and matrices E , too.
- 3.4. In the third version of nonextensive statistical mechanics, magnetization vs. temperature ($M_{A(B)}$ vs. T) for a two spin- $1/2$ system.
- 3.5. Additivities of total energy vs. temperature ($U_{\text{tot.}}$ vs. T) and magnetization vs. temperature ($M_{\text{tot.}}$ vs. T).
- 3.6. For escort distributions, a layout showing the summarized formal derivation from the full Hilbert space to the Hilbert subspaces.
- 3.7. Use of the escort distributions.

- 4.1. For $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$, magnetization vs. temperature measured in a CBPF SQUID.
- 4.2. For $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$, magnetization vs. external magnetic field measured in a CBPF SQUID.
- 4.3. Magnetic entropy curve for $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$.
- 4.4. Experimental magnetization vs. temperature for $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ under low magnetic fields.
- 4.5. For $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$, a comparison between experimental and calculated M vs. T .
- 4.6. For $\text{Pr}_{0.70}\text{Ca}_{0.30}\text{MnO}_3$, computer calculation of magnetization vs. temperature.

LIST OF TABLES

- 4.1. Data used in the CBPF SQUID in measuring $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0.35$ and 0.40 .
- 4.2. For a cubic symmetry, the conventional Stevens operators.
- 4.3. Angular momentum quantum numbers of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$.

ACRONYMS

FHS: Full Hilbert space

HS: Hilbert Subspace

CBPF (Portuguese acronym): Brazilian Center for Research in Physics

SQUID: Superconducting Quantum Interference Device

CMR: Colossal Magnetoresistance

ZFC: Zero Field Cooling

FC: Field Cooling

FOREWORD

The book “Compound Systems in Nonextensive Statistical Mechanics and Manganites”, by F. A. R. Navarro is a material that was actually missing in the literature that treats the interesting field of Nonextensive Statistical Mechanics, as first introduced by C. Tsallis. The subject is extremely rich and has, by now, a vast spectrum of works that cover the area. However, the specific application to compound materials—in this case manganites—opens up new possibilities of learning the topic while considering a relevant category of structures. It is non-trivial application.

The introduction is very well presented and sets up the necessary backgrounds for a pleasant and fluent reading. Navarro is able to pick up the truly relevant points and he presents them with the ability of a long experience in thinking about and teaching the material. It is really a very helpful introduction to fix up the pre-requisites to dive into the interesting chapters that follow up.

The next chapters are more specific, but clear and complete, with the ideas, calculations and discussions presented with remarkable explanations. No doubt that beginners and those who wish to enter the field shall benefit a great deal from the material covered by Navarro’s book. The chapter with the applications is very up-to-date and may provide tools and inspiration for further research.

The Bibliography is good and allows the reader to easily grasp the state-of-art of the research field. Students, young researchers, and more experienced professional may find in the book material that may enrich seminars, lectures, and thesis work.

I deeply recommend Navarro’s book for the high quality of its text, for the outstanding balance of the contents of each chapter and for bringing to light a non-trivial and very appealing framework to apply Tsallis’ nonextensive statistical mechanics.

J. A. Helayël-Neto,
Brazilian Center for Research in Physics
(CBPF).
November 2020.

PREFACE

By this book, I want to divulge two matters, manganites and nonextensive statistical mechanics. They have been my research aims for many years in both the Federative Republic of Brazil and the Republic of Peru. In the former, in the early 2000s, I started a Ph.D. degree in Physical Sciences at the Brazilian Center for Research in Physics, which is located in the Marvelous City of Rio de Janeiro. In the latter, nowadays, I am a tenured professor at the National University of San Marcos in the city of Lima. For many years I wished to write a book on physics; however, because of the duties of everyday life, I postponed that longing.

Before writing this book, I had focused on publishing only scientific papers. Certainly, after obtaining a scientific result, a manuscript requires less time and fewer pages than a regular book does. But now, finally, I have spent my idle hours ordering and updating information about the two aforementioned matters.

Indeed, organizing this book has been a wonderful personal experience. I always liked too much link ideas and words. After reading this book, I hope you, dear reader, will be interested in delving into the issues introduced herein.

Finally, my thanks and gratitude to all who encourage me to move forward with my life as a physicist.

Felipe Américo Reyes Navarro,
Doctor in Physical Sciences,
Lima, Republic of Peru,
August 2021.

INTRODUCTION

This book deals with the application of nonextensive statistical mechanics in compound systems. In particular, the focus is on magnetism and manganese oxides, because these last materials have several important features that enable the application of nonextensive statistical mechanics; in physics, manganese oxides are also named manganites. Nonextensive statistical mechanics, also known as Tsallis statistics, can address the complex problem of manganites in a phenomenological way. Thus, in this book, we will mainly study compound magnetic systems $A + B$. This is motivated because manganites have magnetic manganese presenting two important valence states, Mn^{3+} and Mn^{4+} , that is, forming two magnetic sublattices.

Besides, we will learn nonextensive quasi-probability distributions, which originate from the relaxation of the Tsallis cutoff. These distributions describe well the fall of the magnetization of the $Pr_{1-x}Ca_xMnO_3$ manganite series, i.e., the metastable metal-ferromagnetic phase (at low temperatures with concentration $x = 0.30-0.50$). Similarly, an interesting problem and its solution will be introduced; it is concerning the calculation of mean values of compound systems, in different Hilbert spaces.

Currently, there is rich and varied experimental evidence, as well as excellent approaches in various branches of science, indicating that a nonextensive statistical theory, with a power-law type distribution, provides a solution to several anomalous problems in which Boltzmann-Gibbs-Shannon statistical mechanics fails. Nonextensive statistical mechanics has applications in, e.g., cosmology and gravitation, digital image processing, magnetism, complex systems theory, etc.; the number of publications concerning it is huge. There are more than 8000 publications that study or reference the usually called Tsallis statistics (Website 1, 2022).

Herein, in Part I, Chapter One, a general introduction to the physics of manganites is made, especially for the $Pr_{1-x}Ca_xMnO_3$ series. Thus, the main theories that explain the exotic behavior of these manganese oxides are summarized. We have, for example, the double-exchange model (the original and the current one), the model of polarons, the Anderson localization model, and the phase separation scenario in a percolative process. Likewise, we will find a summary of some models for manganites

from first principles as well as a current overview of nanostructured manganites.

In Part II, in Chapter Two, before the formalism of nonextensive statistical mechanics is introduced, we will review a historical evolution of the ideas that led to the foundation of the statistical concepts and, especially, to the construction of statistical mechanics. Likewise, it is introduced some entropies successfully applied in different areas of science. Afterward, we will deal with nonextensive statistical mechanics; we will learn the following topics: how Tsallis entropy is postulated, the link between Renyi entropy and Tsallis entropy, pseudo-additivity for Tsallis entropy, escort entropies, generalized mean values, three definitions of temperature in that statistical theory, etc. Furthermore, in Chapter Three, we will learn about an alternative method to calculate the mean values for a compound quantum system $A + B$; this method is applicable to *any* theory using a power law, including obviously nonextensive statistical mechanics. Specifically, only for didactic reasons, a two spin- $1/2$ system is studied; the same study can be made for spins 2 and $3/2$, Mn^{3+} and Mn^{4+} spins, respectively. Then, two procedures are utilized to calculate the mean values of the two spin- $1/2$ system: The usual method of partial matrices raised to the entropic index q , ρ_A^q and ρ_B^q , and an alternative method in agreement with the partial trace quantum operation.

In Part III, applications of the topics discussed are explained. Thus, in Chapter Four, for $Pr_{1-x}Ca_xMnO_3$ with $x = 0.30-0.50$, it is introduced a phenomenological and specific model by using the alternative method along with the mean-field approximation. This model works well in studying specific aspects of manganites. Chapter Five summarizes the matters we will deal with.

Furthermore, it is introduced three appendices. In Appendix A, magnetoresistance and the magnetocaloric effect and their applications will be explained. In Appendix B, we will establish several properties of the q -logarithm function (for $q = 1$, we recover the natural logarithm function). Finally, in Appendix C, we will find out several properties of the q -operations (q -sum, q -difference, q -multiplication, and q -division). Likewise, we will discover how to obtain the skewness and kurtosis for both the standard Gaussian distribution and the q -Gaussian distribution.

PART I

MANGANITES

CHAPTER ONE

INTRODUCTION TO THE PHYSICS OF MANGANITES

Manganites are materials that are currently being intensively investigated by the scientific community; special attention is given to perovskite manganites, which have rich and complex physics at the same time. This is due to the electron-lattice and electron-electron interactions as well as the mixed valence of the manganese ions (Mn^{3+} and Mn^{4+}). These features allow the structural, magnetic and transport properties to be intrinsically related to each other.

Another characteristic, important and unusual, that distinguishes these materials: For certain compositions, in the vicinity of a metal-insulator transition, they present magnetoresistance with very large negative values (it is named colossal magnetoresistance, CMR). Certainly, nanostructures are at the heart of CMR; there are also studies of compounds in which similar nanostructures have not been fully understood, for example, high-temperature superconductors and Eu-based semiconductors. In addition to colossal magnetoresistance, manganites have metallic phases with a conduction band having polarized spin (semi-metallic behavior); this last fact is promising for potential technological applications.

A Brief Historical Outlook

Historically, for the first time, the perovskite manganites $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) were studied in the 50s. Because of their experimental studies, using polycrystalline samples, G. H. Jonker and J. H. Van Santen as well as E. O. Wollan and W. C. Koehler are renowned researchers. However, we also have relevant theoretical investigations from C. Zener, P. W. Anderson, and H. Hasegawa as well as P. G. de Gennes. These last researchers developed the double-exchange model to explain the antiferromagnetic-insulator and metal-ferromagnetic states at certain concentrations x . Yet investigations about manganites only boosted with the discovery of colossal magnetoresistance in the middle of the 70s. If we

use the parameter $MR = \frac{R_{(0)} - R_{(H)}}{R_{(H)}}$, we can find magnetoresistance values of 127 000 % at 77 K ($R_{(0)}$ is the zero-field resistance, and $R_{(H)}$ is the resistance having an external field). Besides, if magnetoresistance is expressed via the alternative parameter $mr = \frac{R_{(0)} - R_{(H)}}{R_{(0)}}$, it is about 99 %. In the $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_\delta$ thin films, we can find values of 10^6 %.

General Formula

The most interesting perovskite manganites have the general formula $\text{R}_{1-x}\text{M}_x\text{MnO}_3$, where R is a rare earth metal, trivalent, and M is an alkaline earth metal, divalent, which can be Ca, Sr, Ba, or Pb. The last formula is usually used when we have electron-hole doping. For instance, LaMnO_3 , the mother compound of manganites, has $x = 0$ (no doping) and 100 % of Mn^{3+} ; the calcium doping, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, provokes the pairing of the Mn^{4+} ions, that is, x is associated with divalent cations.

Similarly, if we make an electron doping, we will use $\text{R}_x\text{M}_{1-x}\text{MnO}_3$; for example, CaMnO_3 has $x = 0$ (no doping) and 100 % of Mn^{4+} . The lanthanum doping, $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$, causes the pairing of the Mn^{3+} ions, i.e., x is now associated with trivalent cations. An alternative notation for the general formula, with hole doping, is $\text{R}_{1-x}\text{M}_x\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}\text{O}_3$. Besides, electron doping can be performed on LaMnO_3 , using tetravalent cations like Ce, Sn, and others; so, the construction of diode-type structures $p\text{-La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3/n\text{-La}_{1/2}\text{Ce}_{1/2}\text{MnO}_3$, promising in spintronics, would be feasible.

Crystal Structure

The crystal structure of manganites resembles cubic perovskite, which are mixed oxides with stoichiometry ABO_3 . The perfect cubic perovskite has a formula per unit cell (5 atoms); one feature of these materials is the wide variety of substitutions accepted by its crystal structure. The site A can be occupied by almost 25 chemical elements and the site B by almost 50 (but not all perovskites are oxides: F, Cl, or Br can also take the place of O in the structure).

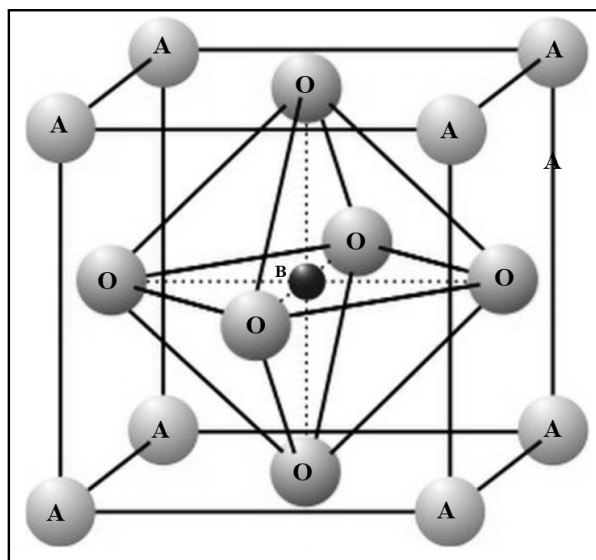


Figure 1.1. Cubic perovskite structure ABO_3 . The gray spheres at the corners represent either rare earth or alkaline earth (A); the black sphere in the body center, a manganese atom (B); and each gray sphere in the middle of each cube face, an oxygen atom (O). This figure was modified from Website 2 (2022).

Figure 1.1 shows the perfect cubic-perovskite structure; concerning oxygen (O), a cation A has dodecahedral coordination, whereas the cation B, octahedral coordination. In this structure, the cation B is surrounded by six oxygen anions, forming the BO_6 regular octahedra so that the B–O–B bond angle is 180° . The deviation from the B–O–B bond angle, for Mn, results in an octahedral tilting as well as a minor overlapping between orbitals; this causes the system to lose its metallic characteristics.

Below a given temperature, compounds ABO_3 have structural transitions reducing their symmetry. In general, perovskites ABO_3 have three types of fundamental distortions: **1)** Displacements of the cations from their equilibrium positions. **2)** The BO_6 octahedral distortion due to, e.g., the presence of a Jahn-Teller ion, such as Mn^{3+} ; what is provoked by the Jahn-Teller effect—named after Emil Jahn and Edward Teller by the 1937 theorem—which can be static or dynamical. The former Jahn-Teller effect occurs when distortion is large, and permanently affects the molecular geometry; in the latter Jahn-Teller effect, distortions are generally smaller. Two possible distortions are associated with the Jahn-Teller effect: Q_2 is an orthorhombic distortion and Q_3 , tetragonal. The change of distances for

the Mn–O bond is the main result of such distortions. **3)** Cooperative rotation of the BO_6 octahedra, because of the reduced size of the cation A. The BO_6 octahedral rotation is known as the GdFeO_3 rotation; it has the space group Pnma .

In the formation of perovskites, a prerequisite is that the cations A and B have the coordination structures already mentioned. Concerning oxides, this precondition sets lower limits for the radii of these cations [A (0.90 Å) and B (0.51 Å)]. Thus, a parameter that governs the crystallography of manganites can be defined, which was done by Goldschmidt et al. in 1926 in a German journal. They expressed their experimental observations in the famous formula of the tolerance factor t , which has the following expression:

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_O}{r_B + r_O}, \quad (1.1)$$

where r_A , r_B and r_O are the ionic radii of the respective elements. Then, $t = 1$ corresponds to a maximum, perfect closely-packed cubic structure. For $t \neq 1$, at low temperatures, manganites have either a rhombohedral symmetry (with space group D_{3d}^6) or orthorhombic symmetry (with space group D_{2h}^6).

Pyrochlore Manganites

Nowadays, the most studied manganites are the ones with a perovskite structure. However, there are also other crystal structures for them. A well-known example is manganites with general formula $\text{X}_2\text{Mn}_2\text{O}_7$ ($\text{X} = \text{Tl}, \text{In}, \text{Y}$). They have a pyrochlore-type crystal structure (with space group $O_h^7, Fd\bar{3}m$). This type of arrangement consists of two sublattices, which respectively have two types of crystallographically different oxygen. Below, the symbol O(1) will indicate the oxygen in the sublattice (1); similarly O(2). Thus, the first sublattice is $\text{MnO}(1)_{6/2}$, which forms octahedrons of oxygen, with manganese in the center, the same as in perovskites, connected to each other in the form of rings. The second sublattice is $\text{X}_2\text{O}(2)$, which passes between the rings formed by the $\text{MnO}(1)_{6/2}$ sublattice. These structures have a global cubic symmetry.

The $\text{Tl}_2\text{Mn}_2\text{O}_7$ manganite is important, as it presents colossal magnetoresistance around the FM-PM transition temperature, $T_C \sim 120$ K. Finally, a well-known fact in the scientific literature: Many pyrochlore manganites have a high geometric-magnetic frustration.

Electronic Structure

For an isolated 3d-transition metal, five degenerate orbital states are available for the 3d electrons with $l = 2$ (the energy levels of the Mn^{3+} orbitals are shown in Figure 1.2). The presence of an oxygen octahedron removes this degeneracy. The five d orbitals are shifted into two degenerate groups: triply degenerate t_{2g} orbitals (d_x , d_y , and d_z) and doubly degenerate e_g orbitals ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$). However, the Mn ion is immersed in a non-cubic crystal field, which removes the degeneracy of the t_{2g} and e_g orbitals. The t_{2g} electrons have a localized character and the e_g electrons, an itinerant character; after an explanation of the double-exchange phenomenon, this will be clearer. For the Mn^{3+} and Mn^{4+} ions, the atomic correlations guarantee a parallel alignment of spins (Hund's first rule). The Mn^{3+} ion presents the electron configuration $3d^4, t_{2g}^3 e_g^1$ with $S = 2$ (everywhere in this book, S stands for spin and S , entropy). According to Hund's rule, this cation can accept the fourth electron as being antiparallel to the other three t_{2g}^3 electrons. But because the exchange energy is around 2.5 eV, which is higher than the crystal field splitting $\delta \sim 1.5$ eV, the fourth electron aligns parallel to the t_{2g}^3 electron, in the e_g orbital (in the lanthanum cobaltite LaCoO_3 , Co^{3+} has six 3d-electrons in the $t_{2g}^{3\uparrow, 3\downarrow}$ orbital). The Mn^{4+} ion presents $3d^3 t_{2g}^3$ with $S = 3/2$.

Main Theories Seeking to Unravel the Physics of Manganites

In the scientific literature, there are several theories that explain the physical properties of manganites. Then, summarizing the best known, we have the following ones: the original model of double exchange, the current model of double exchange, the model of polarons, and the Anderson localization model. In the next section, we will introduce an important model appearing in the scientific literature: the phase separation scenario. In Figure 1.3, we have a conceptual diagram about these theories.

We begin with an introduction to the original model of double exchange, wherein the magnetic properties are dominated by short-range exchange interactions between the spins of Mn—in 1996, E. L. Nagaev proposed a completely different theory, i.e., the charge carriers are holes in the p-band of oxygen.

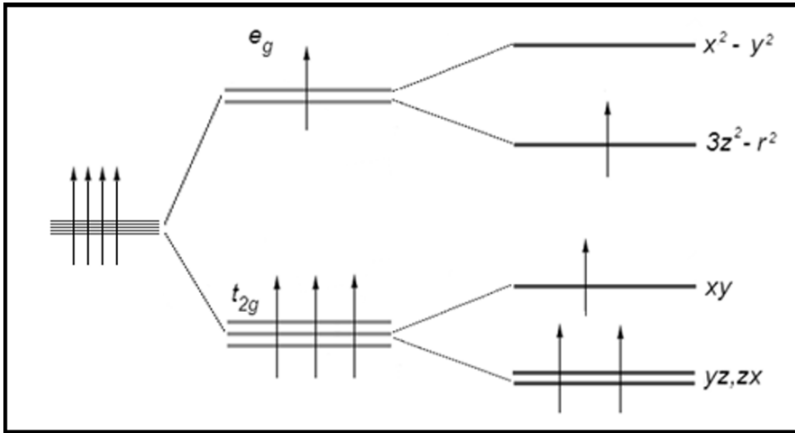


Figure 1.2. Energy Levels of Mn^{3+} . On the left side, we have the case of a free ion; at the center, the levels in the presence of an oxygen octahedron (cubic crystal field); and on the right side, the levels in the presence of a tetragonal crystal field.

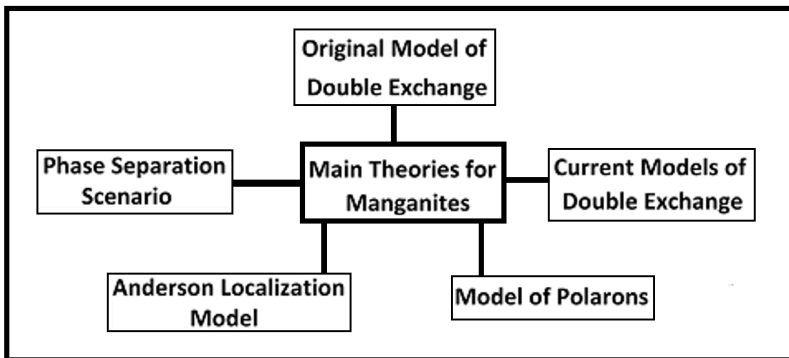


Figure 1.3. Conceptual diagram showing the main theories that explain the properties of manganites.

Such properties are relevant between two spins of manganese separated by an oxygen atom, and they are controlled by the overlapping between manganese's d-orbitals and oxygen's p-orbitals. An interesting case is $Mn^{3+}-O-Mn^{4+}$ in which the Mn ions can exchange their valence, through a jump of the e_g electron of Mn^{3+} into the p-orbital of O, and, simultaneously, another jump of an electron from O to the empty e_g orbital of Mn^{4+} . This

mechanism, called double exchange, was proposed for the first time by the American physicist Clarence Melvin Zener in 1951; it ensures a strong ferromagnetic-type interaction.

Later, in 1955, the American and Nobel Prize in Physics Philip Warren Anderson and the Japanese researcher H. Hasegawa enhanced the ideas of C. M. Zener by introducing the probability of the e_g electron to be transferred from Mn^{3+} to its neighbor Mn^{4+} . Thus, we have the electron mobility formula: $T = T_0 \cos(\theta/2)$, where T_0 symbolizes the hopping integral, and θ represents the angle between spins of localized t_{2g} electrons. $\theta = 0$ corresponds to a ferromagnetic arrangement, with maximum electron mobility, i.e., the probability of the jumps is maximum in $\theta = 0$; it is obtained, therefore, a metal ferromagnetic behavior. Likewise, $\theta = \pi$ corresponds to an antiferromagnetic arrangement; in this case, the conduction e_g -electrons mobility is canceled, that is, we have an antiferromagnetic insulator behavior.

The quantum model analogous to the earlier semiclassical vision was presented in 1972 by the Japanese researchers Kenn Kubo and Nagao Ohata. The competition between the double-exchange ferromagnetism and the superexchange antiferromagnetism gives rise to complex magnetic phase diagrams (superexchange is an indirect exchange interaction in which the separation between ions is greater than, for example, the double exchange). That double-exchange model has been utilized to explain the colossal magnetoresistance phenomenon (however, some authors claim that certain materials—such as pyrochlore manganites and chromium spinels—present colossal magnetoresistance, but not double exchange). For example, the Japanese Nobou Furukawa in 1995, using double exchange, has shown that there is a relationship between resistivity, ρ , and magnetization, M , with a small M/M_{sat} :

$$\frac{\rho}{\rho_0} = 1 - C \left(\frac{M}{M_{sat}} \right)^2, \quad (1.2)$$

where ρ_0 is the resistivity without application of a magnetic field; C , a constant; and M_{sat} , the saturation magnetization.

At present, there are modern models of double exchange. The original meaning of the term *double exchange* has been, in some way, distorted because many scientific studies do not consider the degrees of freedom for oxygen, which exerts a bond between the manganese ions; they consider only manganese Hamiltonians, which can give origin to ferromagnetic phases. Similar models disregarding oxygen are also called double exchange. Usually, in this model, it is indicated that the e_g electron jumps from Mn^{3+} to Mn^{4+} with the extraordinary fact that the electron memorizes

what its value of spin is. The e_g -electron transfer, from Mn^{3+} to Mn^{4+} due to the double exchange, is the basic mechanism of electrical conductivity. In those manganites with a strong double exchange, the e_g electrons are in a ferromagnetic phase, being $x \sim 1/3$ (concerning $R_{1-x}M_xMnO_3$). Meanwhile, the double-exchange model is known to be incomplete in explaining the complex behavior present in the manganese oxides. However, in 2001, by using computer calculations for the double-exchange model, Atsuo Satou and Masanori Yamanaka succeeded to show that the ground state of manganites spontaneously exhibits a self-similarity, that is, a fractal shape; specifically, they found the Cantor set.

The model of polarons is another much-studied model; there is evidence for the existence of polarons in $La_{1-x}Sr_xMnO_3$ with $x = 0.3$ and 0.4 . It has been observed a strong and reversible change of the electronic structure above the Curie temperature. The localization of the charge and an increase in the Mn magnetic moment, as well as Jahn-Teller distortions, are evidence for the formation of the Jahn-Teller polarons. This phenomenon only appears when the sample is heated above the Curie temperature T_C . Those polarons are consistent with a phase separation scenario. However, according to some investigators, the fact that polaron theoretical models are valid at high temperatures—outside the temperature range in which the colossal magnetoresistance occurs—greatly limits these models (Dagotto 2005). Even the complex and small clusters with CE-phases could not be interpreted as a gas of polarons; a CE-phase is the one with charge ordering and mixture of the C- and E- type antiferromagnetism in the insulating state.

Finally, we have the Anderson localization model, which was utilized to explain the insulating state above T_C ; however, the enormous disorder, necessary to obtain the localization in the major densities, is an obstacle to the success of the theory. Moreover, this model does not consider phase competition, a mechanism apparently necessary to explain colossal magnetoresistance. Furthermore, for illustrative purposes, it must be mentioned that this model emerged in 1961 to study a magnetic impurity immersed in a metal matrix. Five years later, John Robert Schrieffer and Peter Adalbert Wolff showed that the Kondo Hamiltonian could be derived from the Anderson model within an appropriate limit. The Kondo model is named after the Japanese theoretical physicist Jun Kondo, who also has studied two-band superconductors and the anomalous Hall effect. Even more, in general, J. Kondo has contributed to understanding the physics of many-body systems and, especially, he has shed light on the study of magnetic phenomena within solid state physics.

Phase Separation Scenario

This scenario has been proposed to explain the complex behavior of manganites. There are dozens of experiments supporting this scenario (by using techniques like electron microscopy, electron transport, nuclear magnetic resonance, neutron diffraction, synchrotron X-ray diffraction, etc.). Thus, there have been observed phases' competition and coexistence. Specifically, it has been reported some mixtures of the following phases: metal and insulator (electronic); ferromagnetic, antiferromagnetic, and paramagnetic (magnetic); and charge and orbital orderings. Phases' competition and coexistence would also arise in superconducting cuprates. There is evidence for the competition between a superconducting phase and a mixture of charge-stripe ordering in $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$.

Even so, some researchers are cautious about the success of this scenario and suggest additional research concerning it; that prudence is due to all basic characteristics of the phase separation are not known currently, for example, the dynamical behavior. Consequently, we have at least three models concerning what the origin of this phase separation is: **1)** electronic-driven phase separation scenario, **2)** phase separation scenario induced by disorder, that is, in a concomitant percolative process, and **3)** strain-driven phase separation scenario.

In respect of the first model, there is theoretical research showing the existence of phase separation between regions rich and poor in the content of charge carriers, that is, with different electron densities. For example, in this context, the one-orbital model and the two-orbital model can be used to study phase separation. The calculation of the e_g -electron density, as a function of the chemical potential, results in discontinuities in the electron density for some values of the chemical potential. This fact is interpreted as the existence of inhomogeneous ground states, separated into regions with different charge densities. Meanwhile, there is also another phase separation scenario in which the electron densities are equal.

With respect to the second model, in a first-order transition in the absence of disorder, the system gets confused and does not know if it is insulating or metallic. However, when the disorder is dominant, fine clusters of the two phases are formed. The competition of the two phases, in the presence of disorder, will finish in larger clusters with equal density. In this second model, the metal-insulator transition and the associated colossal magnetoresistance occur in a percolative and concomitant process of the metal ferromagnetic domains. The aforementioned first-order transition is caused by different charge and magnetic orderings of the phases in competition. Furthermore, the coexistence of metal clusters and

charge-ordered clusters has been experimentally verified; the value of the applied magnetic field determines the size and structure of the previously mentioned clusters.

Concerning the third model, strain is assumed to be the driving force of the phase separation. In this model, lattice distortions are important for manganese oxides. The elementary assumptions in the model are **(a)** the system is metallic when strain is absent, and the same system is insulating when strain is present; **(b)** the system has Jahn-Teller lattice distortions modifying the elastic energy of the system.

Consequently, we can affirm that, nowadays, phase separation is an important process in the physics of manganites. Inherent defects in the sample manufacturing process, such as variations in the oxygen content as well as twinning, could be also behind this phenomenon of phase separation. However, though the phase separation scenario can be separated into disorder-driven or intrinsic electronic, the truth is probably a mixture of both. Therefore, whatever the cause that triggers the formation of clusters and percolation, phases' competition and coexistence constitute the fundamental theory behind (I thank Prof. Elbio Dagotto for his comments that helped me improve this paragraph).

On the other hand, $\text{La}_{\frac{1-y}{2}}\text{Pr}_y\text{Ca}_{\frac{1-y}{2}}\text{MnO}_3$ is considered a prototype material to study the phase separation; for $y = 0$, we have $\text{La}_{\frac{1}{2}}\text{Ca}_{\frac{1}{2}}\text{MnO}_3$, which has a ferromagnetic metal state at low temperatures. For $y = \frac{1}{2}$, we have $\text{Pr}_{\frac{1}{2}}\text{Ca}_{\frac{1}{2}}\text{MnO}_3$, which has an insulating state with charge ordering. Likewise, typical characteristics of the spin-glass state have been found in manganites with phase separation (however, in the $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ single crystals, we have a spin-glass state with orbital ordering but without phase separation). In the $(\text{La}_{0.25}\text{Nd}_{0.75})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ceramic, the origin of magnetic frustration and the spin-glass behavior in the phase separation are very complex; the coupling of a set of interacting magnetic clusters would be sufficient to explain the spin-glass behavior. This behavior can also be attributed to the interaction of clusters within the separate phase state.

Besides, it is also convenient to report upon the model that considers colossal magnetoresistance as a Griffiths singularity. Then, the magnetic transition provokes colossal magnetoresistance; this transition can be considered as some kind of percolation, but these ideas have to be seen within the context of the Griffiths phase, which is a peculiar phenomenon of the disordered systems. Specifically, the Griffiths singularities can be used to explain anomalous aspects of susceptibility and specific heat in the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ single crystal. In classical statistical mechanics, the

Griffiths singularities are considered essential singularities and, therefore, they have no effect on the static properties of the system.

Furthermore, there are two types of colossal magnetoresistance at different temperature intervals. In addition to the standard colossal magnetoresistance, next to T_C , there is another colossal magnetoresistance at low temperatures. Besides, manganites $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.70}\text{Ca}_{0.30}\text{MnO}_3$ have been experimentally used to provide evidence in this regard. Likewise, the neutron diffraction technique, with inelastic scattering, can be used to show the discontinuous nature of the metal-insulator transition induced by an external field. Thereupon, Monte Carlo simulations can be also used to study half-doped manganites.

Charge-Ordering Phase Transition

This one has been known since 1939, when the Dutch chemist Evert Johannes Willem Verwey described, in ferrous ferrite (Fe_3O_4 with spinel structure), the transition from a state with charge ordering to a disordered state, upon exceeding a particular temperature. Verwey assumed that the Fe^{2+} and Fe^{3+} cations are alternately arranged. In the scientific literature, such a transition is known as the Verwey transition. In some transition-metal oxides, this system has also been reported; however, it is in manganites that it has attracted the attention of researchers.

The charge ordering in manganites was observed for the first time in 1955, by E. O. Wollan and W. C. Koehler, who used neutron diffraction in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $0 < x < 1$. In 1985, the charge ordering has been also studied by Jirak et al. by using neutron diffraction in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ with $0 < x < 1$. This phase transition in manganites could be due to the Coulombic interaction, which prevails over the kinetic energy; nonetheless, there is also evidence for the influence of the electron-phonon interaction. The insulating state presents antiferromagnetic stripes of static charges; in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (with $x = 1/2, 2/3, 3/4$, and $4/5$), it has been discovered pairs of octahedral stripes Mn^{3+}O_6 separated by octahedral stripes Mn^{4+}O_6 .

Next, as a didactic example, we can mention $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, for which it is possible to obtain the Mn^{3+} and Mn^{4+} charge ordering below the critical temperature $T_{\text{CO}} = 150$ K (therefore, it has a crystal structure with two classes of the MnO_6 octahedra). In other words, there is a phase transition below T_{CO} , known as Wigner crystallization or Verwey transition. Below T_{CO} , the extra electron of Mn^{3+} orders alternately onto the Mn^{4+} ions (forming a rock salt-type arrangement); besides, above T_{CO} , the sizes of the MnO_6 octahedra are equal, with a manganese valence state