

## Contents

Preface XI

Introduction 1

<b>1</b>	<b>Crystal Chemistry of Cobalt Oxides</b>	<b>3</b>
1.1	Introduction	3
1.2	Stoichiometric Perovskites $\text{LnCoO}_3$	4
1.3	Stoichiometric $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ Perovskites (A=Ca, Sr, Ba)	7
1.4	Oxygen-Deficient Perovskites: Order–Disorder Phenomena in the Distribution of Anionic Vacancies	9
1.4.1	The Perovskites $\text{ACoO}_{3-\delta}$ (A=Ca, Sr, Ba)	9
1.4.2	The Sr-Rich Perovskites $\text{Sr}_{1-x}\text{Ln}_x\text{CoO}_{3-\delta}$	13
1.4.3	The Ordered Oxygen-Deficient 112 Perovskites $\text{LnBaCo}_2\text{O}_{5+\delta}$ and $\text{LnBaCo}_2\text{O}_{5.5+\delta}$	16
1.5	The Ordered Double Stoichiometric Perovskite $\text{LaBaCo}_2\text{O}_6$	18
1.6	Hexagonal Perovskite and Derivatives	19
1.7	The RP-Type Cobaltites: Intergrowths of Perovskite and Rock Salt Layers and Derivatives	22
1.7.1	Single-Layered RP Phases $\text{Ln}_{2-x}\text{AxCoO}_4$ ( $n = 1$ ), with A = Ca, Sr	23
1.7.2	Double-Layered RP Cobaltites: $\text{Sr}_{3-x}\text{Ln}_x\text{Co}_2\text{O}_{7-\delta}$ type	25
1.7.3	RP Derivatives with Double and Triple Rock Salt Layers	29
1.7.4	Tubular Cobaltites	33
1.8	Cobaltites with a Triangular Lattice	34
1.8.1	Spinel Cobaltites	34
1.8.2	$\text{Na}_x\text{CoO}_2$ -Type Lamellar Oxides	37
1.8.3	The Misfit Cobaltites	45
1.8.4	Intergrowth of Hexagonal Perovskite and $\text{CdI}_2$ -Type Layers	50
1.8.5	Kagomé “114” Cobaltites: $\text{LnBaCo}_4\text{O}_{7+\delta}$ and $\text{CaBaCo}_4\text{O}_{7+\delta}$	51
1.8.6	Unidimensional Cobaltite $\text{Ca}_3\text{Co}_2\text{O}_6$	58
1.9	Some Other Original Cobaltites	59
	References	64

<b>2</b>	<b>Electronic and Magnetic Properties of Stoichiometric Perovskite Cobaltites</b>	<b>71</b>
2.1	Stoichiometric LnCoO <sub>3</sub> Perovskites	71
2.1.1	Electronic Structure and Spin State Transition	71
2.1.2	Magnetic Properties of LnCoO <sub>3</sub>	80
2.1.3	Electrical Properties of LnCoO <sub>3</sub>	82
2.1.4	Magnetoresistance in LnCoO <sub>3</sub>	85
2.1.5	Phase Separation in LnCoO <sub>3</sub>	86
2.1.6	Thermoelectric Properties of LnCoO <sub>3</sub>	87
2.1.7	Ferromagnetism in LaCoO <sub>3</sub> Nanoparticles and Thin Films	88
2.2	Stoichiometric SrCoO <sub>3</sub> ; Ferromagnetism and Metallic Conductivity	89
2.3	Stoichiometric Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub> Perovskites (A = Ca, Sr, and Ba)	90
2.3.1	Mixed Valence and Spin State of Cobalt	90
2.3.2	Magnetic Properties of Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub> (A = Ca, Sr, and Ba)	93
2.3.2.1	The Perovskites La <sub>1-x</sub> Sr <sub>x</sub> CoO <sub>3</sub>	94
2.3.2.2	The Perovskites La <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub> (A = Ca and Ba)	97
2.3.2.3	Other Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub> Perovskites	99
2.3.2.4	Half-Doped Systems	102
2.3.2.5	Substitution at Co Sites in La <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub>	103
2.3.3	Transport Properties of Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub>	104
2.3.3.1	The Perovskites La <sub>1-x</sub> Sr <sub>x</sub> CoO <sub>3</sub>	104
2.3.3.2	The Perovskites La <sub>1-x</sub> (Ca/Ba) <sub>x</sub> CoO <sub>3</sub>	106
2.3.3.3	Other Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub> Perovskites	107
2.3.3.4	Substitution at Co Sites in La <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub>	108
2.3.4	Charge Ordering in Ln <sub>0.5</sub> Ba <sub>0.5</sub> CoO <sub>3</sub> Perovskites	109
2.3.5	Magnetoresistance in Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub>	110
2.3.6	Phase Separation in Ln <sub>1-x</sub> A <sub>x</sub> CoO <sub>3</sub>	114
2.3.7	Thermoelectric Power of La <sub>1-x</sub> Sr <sub>x</sub> CoO <sub>3</sub>	118
2.4	The « Ordered » Double Stoichiometric Perovskite LaBaCo <sub>2</sub> O <sub>6</sub>	121
	References	123
<b>3</b>	<b>Electronic and Magnetic Properties of Oxygen-Deficient Perovskite Cobaltites Sr<sub>1-x</sub>Ln<sub>x</sub>CoO<sub>3-δ</sub> and SrCo<sub>1-x</sub>M<sub>x</sub>O<sub>3-δ</sub></b>	<b>129</b>
3.1	Disordered Perovskites	129
3.1.1	Magnetic Properties of the Disordered Perovskites Sr <sub>1-x</sub> Ln <sub>x</sub> CoO <sub>3-δ</sub>	129
3.1.2	Electrical Properties of the Disordered Sr <sub>1-x</sub> Ln <sub>x</sub> CoO <sub>3-δ</sub> Perovskites	135
3.1.3	224 Ordered Oxygen-Deficient Phases and Brownmillerite	137
3.1.4	Magnetoresistance	142
3.1.5	Phase Separation	145
3.1.6	Thermoelectric Properties	146
3.2	Ordered 112 LnBaCo <sub>2</sub> O <sub>5+δ</sub> Perovskites	148
3.2.1	Magnetic Properties	149
3.2.1.1	LnBaCo <sub>2</sub> O <sub>5</sub>	149
3.2.1.2	LnBaCo <sub>2</sub> O <sub>5.5±δ</sub>	149
3.2.2	Electron Transport Properties	161

3.2.2.1	$\text{LnBaCo}_2\text{O}_5$	161
3.2.2.2	$\text{LnBaCo}_2\text{O}_{5.5\pm\delta}$	162
3.2.3	Phase Separation	168
3.2.4	Magnetoresistance	169
3.2.5	Thermoelectric Properties	172
3.2.5.1	$\text{LnBaCo}_2\text{O}_5$	172
3.2.5.2	$\text{LnBaCo}_2\text{O}_{5.5}$	172
	References	175
<b>4</b>	<b>Electronic and Magnetic Properties of Ruddlesden–Poepper-Type Cobaltites</b>	<b>179</b>
4.1	Cobalt Valence and Spin State Transitions	179
4.2	Magnetic Properties of RP Phases	185
4.2.1	The $n = 1$ – RP Cobaltites $\text{Ln}_{2-x}\text{A}_x\text{CoO}_4$	185
4.2.1.1	The Half-Doped RP Phase $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$	186
4.2.1.2	The Magnetic Transition Region Around $\text{LaSrCoO}_4$	187
4.2.1.3	The 2D Ferromagnet $\text{Sr}_2\text{CoO}_4$	190
4.2.1.4	The Sr-Rich $\text{Sr}_{2-x}\text{Ln}_x\text{CoO}_4$ Spin Glass-Like Cobaltites	190
4.2.2	The $n = 2$ RP Cobaltites	192
4.3	Electrical Properties of RP Phases	196
4.3.1	The $n = 1$ RP Phases $\text{Ln}_{2-x}\text{Sr}_x\text{CoO}_4$	196
4.3.1.1	The Half-Doped $\text{Ln}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ Cobaltite	197
4.3.1.2	The $\text{LnSrCoO}_4$ Cobaltites	199
4.3.1.3	$\text{Sr}_2\text{CoO}_4$ and Some Sr-Rich Phases $\text{Sr}_{2-x}\text{Ln}_x\text{CoO}_4$	200
4.3.2	The $n = 2$ RP Phases	201
4.4	Phase Separation in RP Phases	202
4.5	Magnetoresistance of RP Phases	203
4.6	Thermoelectric Properties of RP Phases	206
	References	209
<b>5</b>	<b>Electronic and Magnetic Properties of Cobaltites with a 3D “Triangular Lattice”</b>	<b>211</b>
5.1	The $\text{Co}_3\text{O}_4$ Spinel and Derivatives	211
5.1.1	Valence and Spin States of Cobalt in Bulk $\text{Co}_3\text{O}_4$	211
5.1.2	Magnetic and Transport Properties of Bulk $\text{Co}_3\text{O}_4$ and its Spinel Derivatives	213
5.1.2.1	Magnetic Properties of Bulk $\text{Co}_3\text{O}_4$	213
5.1.2.2	Magnetic Properties of Bulk $\text{Co}_3\text{O}_4$ Spinel Relatives	215
5.1.2.3	Electrical Properties of $\text{Co}_3\text{O}_4$ Spinel	219
5.1.2.4	Magnetoresistance of Cobalt Spinels	221
5.1.3	Magnetic Properties of Nanodimensional $\text{Co}_3\text{O}_4$	221
5.2	The “114” $\text{LnBaCo}_4\text{O}_7$ and $\text{CaBaCo}_4\text{O}_7$ Cobaltites	232
5.2.1	The Cobaltite $\text{YBaCo}_4\text{O}_7$	233
5.2.2	Other $\text{LnBaCo}_4\text{O}_7$ Cobaltites	235
5.2.3	Substitution Effect in $\text{YBaCo}_4\text{O}_7$ at the Cobalt Site	238

5.2.4	The Cobaltite $\text{CaBaCo}_4\text{O}_7$	239
5.2.5	Oxygen Absorption: Oxygen “Hyperstoichiometry” in “114” Cobaltites	241
	References	244
<b>6</b>	<b>Electronic and Magnetic Properties of “Triangular” Layered Cobaltites</b>	<b>249</b>
6.1	The Layer Sodium Cobaltites $\text{Na}_x\text{CoO}_2$	250
6.1.1	Valence and Spin States	250
6.1.2	Magnetic Properties of $\text{Na}_x\text{CoO}_2$ and $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$	251
6.1.3	Electrical Properties of $\text{Na}_x\text{CoO}_2$	258
6.1.4	Influence of Cobalt Charge and Sodium Ordering upon the Transport and Magnetic Properties of $\text{Na}_x\text{CoO}_2$	260
6.1.5	Magnetoresistance of $\text{Na}_x\text{CoO}_2$	261
6.1.6	Thermoelectric Properties of $\text{Na}_x\text{CoO}_2$	262
6.1.7	Phase Separation in $\text{Na}_x\text{CoO}_2$	266
6.1.8	Superconducting Properties of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$	266
6.1.8.1	The Electronic Structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$	268
6.2	Misfit Cobaltites	269
6.2.1	Magnetic Properties of Misfit Cobaltites	269
6.2.1.1	The $n = 3$ Members: “ $\text{Ca}_3\text{Co}_4\text{O}_9$ ” and Relatives	269
6.2.1.2	The $n = 4$ Members of the Bi-A-Co-O Systems (A = Ca, Sr, Ba), and $[\text{Ca}_2\text{Co}_{4/3}\text{Cu}_{2/3}\text{O}_4]_{0.62}\text{CoO}_2$	272
6.2.2	Electrical Properties of Misfit Cobaltites	274
6.2.2.1	The $n = 3$ Members	274
6.2.2.2	The $n = 4$ Members	277
6.2.3	Magnetoresistance of Misfit Cobaltites	278
6.2.3.1	$n = 3$ Misfits	278
6.2.3.2	$n = 4$ Misfits	280
6.2.4	Thermoelectric Properties of Misfit Cobaltites	283
6.2.4.1	$n = 3$ Misfit Cobaltites	283
6.2.4.2	$n = 4$ – Bismuth-Based Misfit Cobaltites	289
6.2.4.3	Mechanism of Thermoelectricity in Misfit and Sodium Cobaltites	290
6.2.4.4	Phase Separation in Misfit Cobaltites	291
	References	292
<b>7</b>	<b>Electronic and Magnetic Properties of the “Unidimensional” Cobaltite <math>\text{Ca}_3\text{Co}_2\text{O}_6</math></b>	<b>297</b>
7.1	Valence and Spin State of Cobalt	297
7.2	Magnetic Properties of 1D- $\text{Ca}_3\text{Co}_2\text{O}_6$ and Related Derivatives	299
7.2.1	Anisotropy	303
7.2.2	Frustration	303
7.2.3	Quantum Tunneling	305
7.2.4	Nanophase	307
7.2.5	Models	307

7.2.6	Effect of Substitution at the Cobalt Sites	309
7.3	Electrical Resistivity of $\text{Ca}_3\text{Co}_2\text{O}_6$ and Derivatives	311
7.3.1	Effect of $\text{Ca}_3\text{Co}_2\text{O}_6$ Doping Upon Resistivity	313
7.4	Magnetoresistance of $\text{Ca}_3\text{Co}_2\text{O}_6$	315
7.5	Thermoelectric Power of $\text{Ca}_3\text{Co}_2\text{O}_6$ and Derivatives	315
	References	318

<b>Index</b>	321
--------------	-----

