Contents

1	Introduction					
	1.1	Overview	8			
	1.2	Electron Correlations	10			
		1.2.1 Mott-Hubbard Insulators	10			
		1.2.2 Zaanen-Sawatzky-Allen scheme	13			
	1.3	Exchange Interaction	17			
		1.3.1 Superexchange	18			
		1.3.2 Double Exchange	19			
	1.4	Jahn-Teller Distortion	21			
	1.5	Charge and Orbital Ordering	23			
	Refe	rence	26			
2	\mathbf{Exp}	perimental Techniques and Setup	29			
	2.1	Soft X-ray Absorption Spectroscopy	29			
		2.1.1 Electron-Photon Interaction in XAS	29			
		2.1.2 Ground State	31			

		2.1.3	Final State	37
		2.1.4	Matrix Element	38
		2.1.5	Linear Dichroism in X-ray Absorption	40
		2.1.6	Examples of XAS	41
	2.2	Exper	imental Setup of XAS	46
	2.3	Epitaz	xial Thin Films Growth in Pulsed Laser Deposition \ldots	53
		2.3.1	Advantage of Pulsed Laser Deposition	53
		2.3.2	Pulsed Laser Deposition System Setup	54
		2.3.3	Epitaxial Growth of $\rm La_{0.5}Sr_{0.5}MnO_3$ Thin Films $\ . \ . \ .$	62
	Refe	erence		66
3	Orb	oital O	rdering of Manganese Oxides	68
3	Or b 3.1	oital O Orbita	rdering of Manganese Oxides al Polarization in LaSrMnO4	68 68
3	Orb 3.1	oital O Orbita 3.1.1	rdering of Manganese Oxides al Polarization in LaSrMnO ₄ Introduction	68 68 68
3	Orb 3.1	Dital O Orbita 3.1.1 3.1.2	rdering of Manganese Oxides al Polarization in LaSrMnO ₄	68686870
3	Orb 3.1	oital O Orbita 3.1.1 3.1.2 3.1.3	rdering of Manganese Oxides al Polarization in LaSrMnO4	 68 68 68 70 71
3	Orb 3.1	oital O Orbita 3.1.1 3.1.2 3.1.3 3.1.4	rdering of Manganese Oxides al Polarization in LaSrMnO ₄	 68 68 68 70 71 77
3	Orb 3.1 3.2	Orbita Orbita 3.1.1 3.1.2 3.1.3 3.1.4 Orbita	rdering of Manganese Oxides al Polarization in LaSrMnO4 Introduction Introduction Theoretical Calculations Experimental Results Conclusion Introduction Introduction	 68 68 68 70 71 77 78
3	Orb 3.1 3.2	Orbita Orbita 3.1.1 3.1.2 3.1.3 3.1.4 Orbita 3.2.1	rdering of Manganese Oxides al Polarization in LaSrMnO4 Introduction Introduction Theoretical Calculations Experimental Results Conclusion Introduction Introduction	 68 68 68 70 71 77 78 78
3	Orb 3.1 3.2	oital O Orbita 3.1.1 3.1.2 3.1.3 3.1.4 Orbita 3.2.1 3.2.2	rdering of Manganese Oxides al Polarization in LaSrMnO4 Introduction Theoretical Calculations Experimental Results Conclusion Al Ordering in La _{0.5} Sr _{1.5} MnO4 Introduction Linear Dichroism	 68 68 68 70 71 77 78 78 81

		3.2.4	Conclusions	90
	3.3	Strain	Induced Orbital Polarization	92
		3.3.1	Introduction	92
		3.3.2	Epitaxial Growth of $La_{0.5}Sr_{0.5}MnO_3$ Thin films \ldots	94
		3.3.3	Polarization-Dependent XAS	96
		3.3.4	LDA+U Calculations	100
		3.3.5	Conclusions	102
	Refe	rence		102
4	\mathbf{Orb}	ital Sy	mmetry of Cobalt Oxides	107
	4.1	Introd	uction of $Na_x CoO_2 \cdots \cdots$	107
	4.2	Funda	mental Issues about $Na_x CoO_2 \dots \dots \dots \dots \dots$	109
	4.3	Polariz	zation-Dependent XAS	111
		4.3.1	Co L-edge XAS	112
		4.3.2	O K-edge XAS	114
		4.3.3	Na K -edge XAS	121
	4.4	Conclu	isions	122
	Refe	rence .		122
5	Con	clusior	a and Future Work	126
	5.1	Conclu	ision	126
		5.1.1	Experimental Setup	126

	5.1.2	Orbital Ordering in $La_{0.5}Sr_{1.5}MnO_4$
	5.1.3	Orbital Polarization in Strained $La_{0.5}Sr_{0.5}MnO_3$ 127
	5.1.4	Orbital Symmetry in $Na_x CoO_2$
5.2	Future	e Work
Refe	erence	
3.2 Refe	erence	9 WOFK

A List of Publications



List of Figures

1.1	A simple 1D electron system.	11
1.2	Energy diagram of a n -electrons system in Hubbard model	12
1.3	Anderson lattice model.	14
1.4	Mott-Hubbard insulator and charge-transfer insulator	15
1.5	Zaanen-Sawatzky-Allen classification scheme	16
1.6	Schematic illustration of superexchange interaction	19
1.7	Jahn-Teller distortion in transition-metal oxides	22
1.8	Orbital ordering in $LaMnO_3$	24
91	K-edge XAS and LDA results of anatase TiO.	33
2.1 2.2	Multiplet spectrum of Ti^{4+} with crystal field	35
2.2	Charge_transfer multiplet in XAS	36
$\frac{2.5}{2.4}$	Core-valence interaction in $L_{\text{redge}} XAS$	38
2.4 2.5	Over $K_{-edge} XAS$ in LaSrMnO.	<i>1</i> 2
$\frac{2.0}{2.6}$	Oxygen K -edge XAS of La ₂ Sr CuO.	43
$\frac{2.0}{2.7}$	Multiplet calculation and Ti^{4+} <i>L</i> -edge XAS	4 0
2.1 2.8	X-ray absorption spectrum of $LaCoO_3$	45
2.9	Detection methods for soft x-ray absorption.	47
2.10	Schematic drawing of the Dragon beamline.	48
2.11	Schematic drawing of x-ray absorption apparatus	49
2.12	Rotary sample holder for LD experimental technique	51
2.13	Pulsed laser deposition system	54
2.14	Schematic drawing of PLD system	58
2.15	Experimental geometry of RHEED experiment.	60
2.16	Formation of a monolayer in RHEED oscillation	61
2.17	Powder XRD of $La_{0.5}Sr_{0.5}MnO_3$	62
2.18	RHEED pattern of $SrTiO_3$ and $La_{0.5}Sr_{0.5}MnO_3$ thin film	63
2.19	RHEED oscillations of epitaxial $La_{0.5}Sr_{0.5}MnO_3$ thin film	63
2.20	XRD of epitaxial $La_{0.5}Sr_{0.5}MnO_3$ thin film	65
3.1	LDA+U calculation of Mn 3d in LaSrMnO ₄	70

3.2	Polarization-dependent O $1s$ XAS of LaSrMnO ₄
3.3	LD spectrum of $LaSrMnO_4$
3.4	Calculated LD spectra of Mn^{3+} cation
3.5	Crystal structure and physical properties of $La_{1-x}Sr_{1+x}MnO_4$. 79
3.6	Charge ordering in $La_{0.5}Sr_{1.5}MnO_4$
3.7	Orbital ordering in $La_{0.5}Sr_{1.5}MnO_4$
3.8	Linear dichroism in Mn <i>L</i> -edge XAS of $La_{1-x}Sr_{1+x}MnO_4$ 83
3.9	Temperature-dependent LD of $La_{0.5}Sr_{1.5}MnO_4$ 85
3.10	O K-edge XAS of $La_{1-x}Sr_{1+x}MnO_4$
3.11	Charge-density contours of $La_{0.5}Sr_{1.5}MnO_4$ 88
3.12	Jahn-Teller distortion of Mn^{3+} in $La_{0.5}Sr_{1.5}MnO_4$
3.13	Spin structures and ferro-orbital ordering of $La_{0.5}Sr_{0.5}MnO_3$. 93
3.14	Reciprocal-space mapping XRD of $La_{0.5}Sr_{0.5}MnO_3$ 94
3.15	Mn $2p$ XAS spectra of La _{0.5} Sr _{0.5} MnO ₃
3.16	O K-edge XAS of $La_{0.5}Sr_{0.5}MnO_3$ 99
3.17	LDA+U of C-type AFM in $La_{0.5}Sr_{0.5}MnO_3$ thin films 101
4 1	
4.1	Crystal structure of $Na_x CoO_2$
4.2	Phase diagram of $Na_x CoO_2$
4.3	Isotropic Co L -edge XAS of Na _{0.5} CoO ₂
4.4	Co $L_{2,3}$ -edge XAS of various doping Na _{0.5} CoO ₂
4.5	O 1s XAS spectrum of $Na_{0.5}CoO_2$
4.6	Doping-dependent O K -edge XAS of Na _x CoO ₂
4.7	Polarization-dependent O 1s XAS of $Na_{0.5}CoO_2$
4.8	Doping-dependent isotropic O 1s XAS of $Na_x CoO_2$
4.9	Na K -edge XAS of Na _x CoO ₂

List of Tables

2.1	Electronic configuration in <i>L</i> -edge x-ray absorption with dipole		
	selection rule.	39	
2.2	Operating Wavelengths of Excimer Laser	56	
2.3	Transmittance Range of Various Materials	57	

