## Contents

1.	The	e Relevance and Historical Development of LEED	1
	1.1	The Relevance of Surface Crystallography	1
	1.2	The Historical Development of LEED	3
		1.2.1 The Period Before Wave Mechanics	3
		1.2.2 The Discovery of Electron Diffraction	4
		1.2.3 The Aftermath of the Discovery of Electron Diffraction	5
		1.2.4 The Period 1930 – 1965	6
		1.2.5 The Renaissance of LEED: Experimental Advances in the	
		Mid-1960s	7
		1.2.6 The Theoretical Solution: The Late 1960s and Early 1970s	7
		1.2.7 The Era of Structural Determination: The 1970s and 1980s	9
2.	The	ELEED Experiment	13
	2.1	General Features of LEED Experiments	14
	2.2	Sample Mounting	14
	2.3	Electron Gun and Display System	18
		2.3.1 Electron Gun	18
		2.3.2 Display System	20
	2.4	Methods of Data Acquisition	21
		2.4.1 Faraday-Cup Collector and Spot Photometer	21
		2.4.2 Photographic Technique	23
		2.4.3 Vidicon Camera Method	24
		2.4.4 Position-Sensitive Detector	27
	2.5	Instrumental Response Function	27
		2.5.1 Basic Concepts	27
		2.5.2 Contributions to the Response Width	29
	2.6	Determination of Angle of Incidence	34
		2.6.1 Different Methods	34
		2.6.2 Theory	35
		2.6.3 An Example	38
	2.7	Determination of the Debye Temperature	41
		2.7.1 The Debye Temperature Normal to the Crystal Surface	42
		2.7.2 The Debye Temperature Parallel to the Crystal Surface	45
3.	Ord	lered Surfaces: Structure and Diffraction Pattern	47
	3.1	Two-Dimensional Periodicity and the LEED Pattern	47
		3.1.1 Miller and Miller-Bravais Indices	47

		3.1.2	Lattice and Basis	48
		3.1.3	Direct and Reciprocal Lattices	49
	3.2	Superl	attices at Surfaces	51
	3.3	Steppe	d and Kinked Surfaces	57
		3.3.1	The Step Notation	57
		3.3.2	The Microfacet Notation for Cubic Materials	59
		3.3.3	Unit Cells of Stepped and Kinked Surfaces	62
	3.4	Symme	etries and Domains at Surfaces	64
		3.4.1	Symmetries in Two Dimensions	64
		3.4.2	Domains	67
	3.5	Interp	retation of LEED Patterns	70
		3.5.1	Patterns with a Bravais Array of Spots	71
		3.5.2	Patterns with Multiple Bravais Arrays of Spots – Domains	74
		3.5.3	Patterns Exhibiting Extinctions Due to Glide-Plane	
			Symmetry	76
		3.5.4	Rationally Related Lattices and Coincidence Lattices	77
		3.5.5	An Instructive Example of Pattern Interpretation	80
		3.5.6	Incommensurate Lattices	82
		3.5.7	Split Spots	84
		3.5.8	An Example: Compact Structures vs. Antiphase Domain	
			Structures of Adsorbed Carbon Monoxide Overlayers	88
		3.5.9	Patterns with Multiple Specular Spots	89
		3.5.10	Laser Simulation of LEED Patterns	89
2				01
4.	Kin	ematic	LEED Theory and its Limitations	91
	4.1		A termis Scottering Easter	92
		4.1.1	Floatic Scattering	92
		4.1.2	Amplitude of Diffraction	92
		4.1.5	Surface Sonaitivity	93
		4.1.4	From Amplitudes to Intensities of Diffraction	93
	1 2	4.1.5	nomatic Structure Easter for Ordered Surfaces	05
	4.2	1 NC KI	Two Dimensional Bragg Conditions	95
		4.2.1	General Derivation of Two-Dimensional Bragg Conditions	95
		4.2.2	in LEED from the Schrödinger Equation	98
		123	Plane Wayes Reams and the LEED Pattern	00
		4.2.3	I-V I-A L <sub>m</sub> and Other Collections of Data	102
		4.2.4	Kinematic Diffraction by Bravais I attices of Atoms	102
		4.2.5	The Case of Non-Bravais Lattices	105
		4 2 7	Surface Structures Deviating from the Bulk Structure	107
		4.2.8	Surfaces with Superlattices	108
		4.2.9	Modulated Structures	108
		4.2.10	The Simple Effect of Multiple Scattering on LEED Patterns	110
		4.2.11	The Ewald Sphere	110
		4.2.12	Further Applications of the Kinematic Theory of LEED	114

	4.3 The Scattering Processes in LEED			116		
		4.3.1	Inelastic Scattering Processes	116		
		4.3.2	Modeling the Effect of the Mean Free Path	117		
		4.3.3	Spin Effects	120		
	4.4	The El	lastic Scattering Potential	120		
		4.4.1	Atomic Potentials	121		
		4.4.2	The Muffin-Tin Constant	122		
		4.4.3	Potential Steps	124		
	4.5	Atomi	c Scattering	124		
		4.5.1	Spherical-Wave Scattering	125		
		4.5.2	Plane Wave Scattering	126		
		4.5.3	Phase Shifts	127		
		4.5.4	Atoms as Point Scatterers	130		
	4.6	The In	ner Potential and the Muffin-Tin Constant	132		
	4.7	Tempe	erature Effects	132		
		4.7.1	The Debye-Waller Factor	134		
	4.8	From	Kinematic to Dynamical LEED	136		
		4.8.1	Clean Crystals and Bragg Reflections in One Dimension	137		
		4.8.2	Three-Dimensional Effects	142		
		4.8.3	Overlayer Effects	143		
5.	Dyr	namica	I LEED Theory	145		
	5.1	Multip	ble Scattering	145		
	5.2	Diffra	ction in Crystalline Lattices	146		
		5.2.1	Expansion in Spherical Waves	147		
		5.2.2	Expansion in Plane Waves	147		
		5.2.3	Expansion in Bloch Waves	148		
		5.2.4	Forward vs. Backward Scattering	149		
	5.3	Multiple Scattering in the Spherical-Wave Representation –				
		Self-C	Consistent Formalism	150		
		5.3.1	Scattering by Two Atoms	150		
		5.3.2	Scattering by N Atoms	153		
		5.3.3	One Periodic Plane of Atoms	154		
		5.3.4	Several Periodic Planes of Atoms	155		
		5.3.5	Change to Plane-Wave Amplitudes	156		
		5.3.6	Layer Diffraction Matrices for Plane Waves	157		
		5.3.7	One-Center Expansion	160		
	5.4	Pertur	bation Expansion of Multiple Scattering in the Spherical-			
		Wave	Representation: Reverse-Scattering Perturbation (RSP)			
		Metho	od	161		
		5.4.1	The Principle of RSP	161		
		5.4.2	The Formalism of RSP	163		
		5.4.3	The Use of RSP	163		
	5.5	Diffra	action by a Stack of Layers: Transfer-Matrix and Bloch-Wave	100		
		Metho	od	104		

		5.5.1 The Bloch Condition		1
		5.5.2 The Bloch Functions		5
		5.5.3 The Transfer Matrix		5
		5.5.4 Wave Matching at the Surface		7
		5.5.5 Small Layer Spacings		3
		5.5.6 Relation to Band Structure		3
	5.6	Diffraction by a Stack of Layers: Layer-Stacking and Lay	yer-	
		Doubling Method		)
		5.6.1 The Case of Two Layers		)
		5.6.2 The Case of Many Layers		l
	5.7	Diffraction by a Stack of Layers: Renormalized-Forward	-	
		Scattering (RFS) Perturbation Method		2
		5.7.1 The Principle of RFS		2
		5.7.2 The Formalism of RFS		2
	5.8	Efficiency of Computation and the Combined-Space Method	od 174	1
	5.9	Superlattices and Domains		5
		5.9.1 Diffraction and Superlattices	175	5
		5.9.2 Domains		3
	5.10	Symmetries	179	)
		5.10.1 Types of Symmetry	179	)
		5.10.2 The Formalism of Symmetrization	180	)
		5.10.3 Glide-Plane Symmetry	181	l
	5.11	Thermal Effects	183	3
		5.11.1 Temperature-Dependent Phase Shifts	184	ŧ
		5.11.2 Illustrations of Multiple-Scattering Effects	100	_
		in Temperature-Dependent LEED		)
	5.12	2 Potential Steps, Surface States, Surface Resonances and LEED		
		Fine Structure		5
		5.12.1 Potential Steps		5
		5.12.2 Surface States, Surface Resonances and LEED Fil	100	•
	5 A 3			,
	5.13	Relativistic and Spin-Dependent Effects in LEED		2
	5.14	Some Other Theoretical Techniques		) <
		5.14.1 Bootstrapping	106	, ;
		5.14.2 The Chain Method	107	, 1
		5.14.4 Readopotentials	198	2
		5.14.5 A Semiclassical Theory of LEED	190	, )
	5 1 5	Outstanding Theoretical Problems in LEED	200	)
	5.15	Application of LEED Theory to Other Electron Spectrosco	nies 201	í
	5 17	Computer Programs	202	,
	5.17			
6.	Meth	ods of Surface Crystallography by LEED	205	;
	6.1	The Kinematic Approach to Surface Crystallography	206	,
		6.1.1 Kinematic Simulation of Intensity Data	206	)

		6.1.2	Layer Spacings from Sequences of Bragg Peaks	208
	6.2	Avera	ging Methods	209
		6.2.1	Constant-Momentum-Transfer Averaging (CMTA)	209
		6.2.2	CMTA with Azimuthal Averaging at Constant Energy	211
	6.3	Fourie	er-Transform Methods	214
		6.3.1	The Patterson Function	214
		6.3.2	The Convolution-Transform Method	219
		6.3.3	The Transform-Deconvolution Method	226
		6.3.4	Fourier Transform of Intensity Beats from Overlayer and	
			Substrate	227
	6.4	The D	ynamical Approach to Surface Crystallography	231
		6.4.1	Dynamical Effects on Intensity Data	232
		6.4.2	Information Content of Measured Data	233
		6.4.3	Extraction of Structural Information	
			from Dynamical LEED Intensities	234
	6.5	Reliab	vility Factors (R-Factors)	237
		6.5.1	Various R-Factors	238
		6.5.2	Reliability of Reliability Factors	244
		6.5.3	Dealing with Different Experiments and Different Beams .	244
		6.5.4	Noise and Smoothing	245
		6.5.5	The Use of R-Factors	246
	6.6	Accur	acy and Precision of Structural Determination	251
7	Dasu	lts of S	tructural Analyses by LEFD	254
7.	7 1	Clean	Unreconstructed Surfaces	254
	/.1	7 1 1	The Rh(111) Surface	258
		712	Multilaver Relaxations	260
	72	Recon	istructed Surfaces	262
		7.2.1	The Ir(110)-(1 × 2) Reconstructed Surface	265
		7 2 2	The Si(100)- $(2 \times 1)$ Reconstructed Surface	273
		723	The GaAs(110)-(1 $\times$ 1) Reconstructed Surface	278
	7.3	Adsor	bed Atomic Lavers	285
	1.0	7.3.1	The $Ir(110)-(2 \times 2)-2S$ Atomic Overlayer	290
		7.3.2	The Ir(110)-c(2 $\times$ 2)-O and Ir(111)-(2 $\times$ 2)-O Atomic	
		1.5.2	Overlayers	294
		7.3.3	The Ti(0001)- $(1 \times 1)$ -N Atomic Underlayer	303
	7.4	Adsor	bed Molecular Layers	305
		7.4.1	The Ni(100)-c( $2 \times 2$ )-CO Molecular Overlayer	309
		7.4.2	The Pd(100)-(2]/ $2 \times 1/2$ )R45°-2CO Molecular Overlayer .	312
		7.4.3	Molecular Overlayers of $C_2H_2$ and $C_2H_4$ on Pt(111) and	
			Rh(111)	314
0	<b>T</b>	Dimo	ncianal Andar Disorder Phase Transitions	318
ō.	1W0	Intro	luction to Order-Disorder Phase Transitions at Surfaces	319
	0.1		Chemisorntion and Ordering Principles	319

		8.1.2	Universality, Nonuniversality, Critical Exponents and	
			Scaling	321
	~ •	8.1.3	Applicability to Actual Surfaces	325
	8.2	The I	nteraction of Hydrogen with the (111) Surface of Nickel	325
		8.2.1	An Optimum Case	325
		8.2.2	Experimental Results for Hydrogen Chemisorption on	
			Ni(111)	326
		8.2.3	Parameters for LEED Analysis	330
		8.2.4	The Geometry of Chemisorbed Hydrogen on Ni(111)	331
		8.2.5	Thermal Motion and Disorder in the Hydrogen Overlayer	335
		8.2.6	The Order-Disorder Phase Transition and Adatom-Adatom	
		0.0.7	Interaction Energies	339
		8.2.1	A Renormalization-Group Theory Description of the	
		0.00	Order-Disorder Transition of Hydrogen on Ni(111)	342
		8.2.8	A Cluster-Variational Description of the Order-Disorder	
		0 2 0	I ransition of Hydrogen on Ni(111)	343
		8.2.9	An Atomic Band Structure Description of Hydrogen on	
	0 7	Thal	N1(111)	345
	0.3	0 2 1	Significance of the U (Dd(100) Surface of Palladium	348
		0.3.1	An Experimental Characterization of Hudroson or	348
		0.3.2	All Experimental Characterization of Hydrogen on Pd(100)	240
		822	The Order Disorder Phase Transition	349
		0.3.3	The Connection Potween the Joing Model and the Lettice	354
		0.3.4	Gas Model	256
		825	The Lattice Cas Model with First and Second Neighbor	300
		0.5.5	Interactions	250
		836	Effects of Three-Body Interactions	360
		837	Effects of Third-Neighbor Interactions	362
		838	Comparison Between Experiment and Theory for	502
		0.5.0	Hydrogen on Pd(100)	364
	8.4	The Ir	interaction of Hydrogen with the (110) Surface of Iron	367
		8.4.1	Significance of the H/Fe(110) System	367
		8.4.2	An Experimental Characterization of Hydrogen on	501
			Fe(110)	367
		8.4.3	LEED Observations and Order-Disorder Phase Transitions	
			of Hydrogen on Fe(110)	369
		8.4.4	Theoretical Predictions: A Lattice Gas	
			on a Centered-Rectangular Lattice	372
		8.4.5	Comparison Between Experiment and Theory	
			for Hydrogen on Fe(110)	376
9.	Che	mical R	eactions at Surfaces and LEED	378
	9.1	Monit	oring Surface Reactions by LEED	378
	9.2	The A	dsorption of Oxygen on Rh(111) at 335 K	379

		9.2.1	First-Order Langmuir Adsorption	380
		9.2.2	The Structure of Oxygen on Rh(111)	382
		9.2.3	LEED Intensity Proportional to Oxygen Coverage	384
	9.3	The R	eaction Between Hydrogen and Ordered Oxygen on	
		Rh(11	1)	386
		9.3.1	Reaction Threshold Temperature	386
		9.3.2	First-Order Catalytic Reaction	386
		9.3.3	Model for the Catalytic Reaction	387
		9.3.4	Activation Energies and Preexponential Factors	389
		9.3.5	Experimental Determination	391
	9.4	The R	eaction Between Hydrogen and Both Ordered and	
		Disord	lered Oxygen on Rh(111)	395
		9.4.1	Order-Dependent Kinetics	395
		9.4.2	Relative Amounts of Ordered and Disordered Oxygen	396
10.	Islan	d Form	nation of Adspecies and LEED	398
	10.1	The Na	ature of Islands on Surfaces	398
	10.2	LEED	Beam Profiles for Arrays of Ordered Islands	399
		10.2.1	Distributions of Islands	399
		10.2.2	One-Dimensional Overlayers	401
		10.2.3	Two-Dimensional Overlayers	403
		10.2.4	Dependence on Surface Coverage	407
		10.2.5	Summary of Theoretical Results for Beam Profiles	410
	10.3	Island	Formation in a Real System: CO on Ru(0001)	411
		10.3.1	Conditions of Island Formation	411
		10.3.2	Experimental Results	411
		10.3.3	Analysis and Discussion of Results	419
			10.3.3a The Step-Limited Model of Island Formation	419
			10.3.3b Dissolution of Islands	422
		10.3.4	Summary of Island Formation Properties for	
			CO/Ru(0001)	426
11.	The	Future	of LEED	427
	11.1	Experi	mental Outlook	427
		11.1.1	Improvements in Experimental Techniques	427
		11.1.2	New Experimental Directions	429
	11.2	Theore	etical Outlook	431
		11.2.1	Survival of the Kinematic Theory	431
		11.2.2	Partial Multiple Scattering	432
		11.2.3	Developments in the Dynamical Theory	433
			11.2.3a Coherent Kinematic Summation of Amplitudes	
			over Different Local Configurations	434
			11.2.3b Reduced Unit Cell	435
			11.2.3c Asymptotic Regime	435
		11.2.4	New Directions	436

11.3 Progress in Structural Determination	438
11.3.1 Degree of Completeness of Structural Determinations	438
11.3.2 R-Factors and Structural Search Techniques	439
11.3.2a Projection Improvement	440
11.3.2b Functional Fitting of R-Factors	442
11.3.2c Steepest Descent	442
11.3.2d Least Squares	442
11.4 LEED vs. Other Surface-Sensitive Techniques	443
11.4.1 Individual Techniques	444
11.4.2 Comparisons Between Surface-Sensitive Techniques	460
11.4.3 Complementary and Competitive Techniques	464
12. Reference List and Table for Surface Structures	467
Appendix A: Acronyms of Techniques Related to Surface Science	525
Appendix B: A Computer Program to Determine the Angle of Incidence	
in LEED	529
List of Major Symbols	545
References	549
Subject Index	587