MICROSTRUCTURES AND STRUCTURAL DEFECTS IN HIGH-TEMPERATURE SUPERCONDUCTORS

This page is intentionally left blank

MICROSTRUCTURES AND STRUCTURAL DEFECTS IN HIGH-TEMPERATURE SUPERCONDUCTORS

Zhi-Xiong Cai & Yimei Zhu

*Brookhaven National Laboratory
Upton, New York, USA*

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**MICROSTRUCTURES AND STRUCTURAL DEFECTS IN
HIGH-TEMPERATURE SUPERCONDUCTORS**

Copyright © 1998 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 981-02-3285-3

Printed in Singapore by Uto-Print

For
Danning and Eriko

This page is intentionally left blank

Preface

This book is geared toward upper-level undergraduate students and entry-level graduate students majoring in physics or materials science who are interested in crystal structure and structural defects, particularly those related to high-temperature superconductors. Researchers involved in studying high- T_c materials should also find the book useful as it consistently summarizes the recent progress in this field.

The book has an extensive introduction to microstructures and structural defects in high-temperature superconductors. It emphasizes the application of experimental as well as theoretical modeling techniques to the study of these complex materials, rather than simply presenting the results of current research. The reader is given an overview of the complexities in understanding structure-sensitive properties of bulk high- T_c materials, such as the transport properties, and in developing large-scale (high current, high field) applications. Whenever feasible, the effects of defects on the superconducting properties of these materials are described to put the study of the microstructure in a proper perspective.

We do not attempt to cover all aspects of high-temperature superconductivity research; instead, only the bare-bone knowledge of superconductivity theory is introduced. To link the structure to the properties, we focus on the interpretation of the microstructure and structural defects based on observations with advanced transmission electron microscopy coupled with theoretical modeling techniques. We illustrate experimental and theoretical techniques to study microstructures and structural defects with examples drawn from various high- T_c superconductors. The usefulness of most of the techniques is not unique to

high-temperature superconductors; they can be easily applied to metals, ceramics, and other complex materials.

This book is mainly derived from our own researches, and is our joint effort. In Chapters 1 (Cai) we briefly review the history of research in high-temperature superconductivity. In Chapter 2 (Cai) we introduced the basic notion of superconductivity and its relationship to microstructure and defects, especially in high- T_c superconductors. Chapter 3 (Cai and Zhu) is an overview of experimental techniques and theoretical modeling, mainly those used in the researches described in this book to study defects in materials. Chapter 4 (Zhu and Cai) summarizes the crystal structure of three major families of high-temperature superconductors, the La-, Y-, and Bi-based cuprates. In Chapter 5 (Zhu), we introduce the basic notions of various types of defects, both intragranular and inter-granular that appear in superconducting oxides, and the geometrical approach (interfacial dislocations and Coincidence-Site-Lattice model) to studying grain boundaries. In the following chapters, we discuss experimental and theoretical studies of various types of microstructural features and defects in high-temperature superconductors. Chapters 6 and 7 are devoted to oxygen disorder/order related defects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Chapter 6 (Cai and Zhu) describes in detail the “tweed” structure, a displacive modulation due to oxygen ordering, and its structural origin. Chapter 7 (Zhu) offers observations and interpretations of the atomic structures of twinning variants and varied twin boundaries, another type of oxygen ordering associated with high-symmetrical lattice planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Chapter 8 (Cai and Zhu) discusses structural modulations and the related phase transformations in $\text{La}_{2-x}\text{Ba}_x\text{O}_4$. Chapter 9 (Cai and Suenaga) covers the kinetics of grain alignment and formation of Bi-2223 in Bi-2223/Ag tapes, which is very important to large-scale applications of the high- T_c superconductors. Chapter 10 (Zhu) presented a novel diffraction technique to study charge distribution in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and Bi-2212 superconductors. Chapter 11 (Zhu) and Chapter 12 (Zhu) extensively discuss the structure of grain boundaries. The former describes various experimental methods based on nano-probe electron microscopy that is required to study grain boundaries, such as determining boundary crystallography and measuring local hole concentration and lattice parameters. The latter provides a detailed account of grain boundary structure including

misorientation distribution in practical Y- and Bi-based superconducting materials. We emphasize the correlation between the boundary hole concentration and the boundary lattice constraint for YBCO, and address the structure-property relation by examining the structure of the electromagnetically characterized Bi-2212 bicrystals. In the last section (12.4) of the chapter (Cai), we propose a theoretical model for understanding superconductivity in polycrystalline materials. In Chapter 13 (Zhu, Sec.13.4: Cai) we present our study of columnar defects produced by heavy-ion irradiation, the effects of crystal orientation, stoichiometry, and imperfection on these columnar defects, and their structural nature and formation mechanism. Brief conclusions are given in the final chapter (Cai), and suggestions made on the future directions of research.

We have tried to treat the subject in an elementary way. While the inclusion of some mathematical formulae is unavoidable, we have emphasized the physics, instead of fancy mathematical treatment. Thus, the reader needs only basic knowledge of statistical mechanics, solid-state physics and calculus to follow the discussions in this book.

It is our hope that this book will draw attention to the area of materials science in which fruitful researches are being conducted and in which many challenging problems remain.

This book has developed over a number of years of research in the Materials Science Division, Department of Applied Science at Brookhaven National Laboratory. We have benefited greatly from the input of our colleagues, visiting scientists, collaborators, students, and friends, who have directly and indirectly contributed to this book. In particular we wish to thank M. Suenaga and D.O. Welch, BNL, who encouraged us to take up this project, for their knowledge, and stimulating discussions. We thank J. Taftø, Univ. of Oslo, for his creative and fruitful contribution during his short but productive summer visits in the recent years. We gratefully acknowledge the generous assistance and cooperation of Q. Li, A.R. Moodenbaugh, R.L. Sabatini and L. Wu. We are also indebted to W. Bian, R.C. Budhani, Y. Corcoran, J. Cowley, Y. Fukumoto, A.G. Khachaturyan, A. King, T.R. Thurston, Y.N. Tsay, J.-Y. Wang, Y.-L. Wang, Z.L. Wang, H.J. Wiesmann, Y. Xu, H. Zhang and J.M. Zuo (in alphabetical order), who are the co-authors of our published researches. We thank F. Ling, Y. Koh, and S. Patt

from World Scientific Publishing Inc. for their help in preparing the manuscript. Last, but not least, we thank our families, Danning and Yida, and Eriko and Anna. This book would never have been written without their understanding and support.

Zhi-Xiong Cai
Yimei Zhu

Long Island, New York
February 1998

Contents

Preface	vi
1 Introduction	1
2 Defects and Superconductivity	7
2.1 What is Superconductivity?	7
2.2 The Electromagnetic Properties of Superconductor . . .	9
2.3 The London Model	10
2.4 Ginzburg-Landau Theory	14
2.5 Two Types of Superconductors	18
2.6 Critical Current in Type-II Superconductors	23
2.7 Flux-line Pinning and Microstructure	24
2.8 Good and Bad Defects	25
3 Tools Used to Study the Defects	27
3.1 Introduction	27
3.2 Experimental Tools	27
3.2.1 Transmission Electron Microscopy	27
3.2.2 X-ray and Neutron Diffraction	30
3.3 Theoretical Modeling and Computer Simulation	31
3.3.1 Interaction Between Atoms	31
3.3.2 Computer Simulation	34
4 The Structure Characteristics	41
4.1 Introduction	41
4.2 Crystal Structure	41
4.2.1 La ₂ BaCuO ₄ and Related Structures	42
4.2.2 YBa ₂ Cu ₃ O _{7-δ} (Y123) and Related Structures . .	44

4.2.3	$\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+6}$ and Related Structures . . .	48
4.3	Bonding and Structural Features	52
5	Types of Defects	55
5.1	Intragranular Defects	55
5.1.1	Point Defects	55
5.1.2	Line Defects-Dislocations	58
5.1.3	Planar Defects	61
5.1.4	Volume Defects - Inclusions	62
5.1.5	Structural Modulations	64
5.1.6	Artificially Created Defects	65
5.2	Intergranular Defects – Grain Boundaries	69
5.2.1	The Concept of Coincidence Site Lattice	70
5.2.2	The Concept of O-lattice	72
5.2.3	Frank Formula	73
6	Oxygen Ordering Related Defects in $\text{YBa}_2\text{Cu}_3\text{O}_7$	75
6.1	Introduction	75
6.2	Models for Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	77
6.3	Effect of Thermal Quenching on Oxygen Ordering	89
6.4	[110] Tweedy Modulation	96
6.5	Theoretical Model for Fe Doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and Tweed	107
6.5.1	Model for Oxygen Ordering in Fe Doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	107
6.5.2	Modification of the Lattice Gas Model to Include Elastic Strain	113
6.6	Reduction and Reoxidation in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$	120
6.7	Three Dimensional Structural Modulation	131
6.7.1	$0.02 < x < 0.10$	131
6.7.2	$0.10 < x < 0.33$	134
6.7.3	Simulation of Tweed Image Contrast	142
6.8	Summary	145
7	The Twin Boundary Structure in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	147
7.1	Introduction	147
7.2	Gross Features of the Twin Boundary	149
7.2.1	Conventional TEM Observations	149

7.2.2	HREM Observations	153
7.2.3	The Effects of Cation Substitution	156
7.2.4	The Effects on Superconducting Properties	159
7.3	Studies of the Displacement at the Twin Boundary	160
7.3.1	Evolution of the Twin-Boundary Structure During Electron-Beam Irradiation	160
7.3.2	The Variability of the Twin Boundaries	162
7.3.3	Analyses of Fringe Contrast of the Twin Boundary	166
7.3.4	Analyses of the Streaks of Diffuse Scattering	170
7.3.5	Interfacial Energy of the Twin Boundaries	174
7.4	Crystallographic Analysis of the Twin Boundary	177
7.4.1	A $\Sigma 64$ Coincidence Boundary	177
7.4.2	Twin-Boundary Steps and Twinning Dislocations	179
7.4.3	A Displacement-Shift-Complete-Lattice (DSCL) Treatment	183
7.4.4	Structure of Mixed Twin Boundaries	185
7.5	Twin Tip	188
7.5.1	Four Twinning Variants	190
7.5.2	The Shape of a Tapered Twin	195
7.5.3	Interfaces of the Orthogonally Oriented Twins	199
7.6	Summary	201
8	Structural Modulation in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$	203
8.1	Introduction	203
8.2	Consecutive Structural Transformation and Lattice Dynamical Model	205
8.3	Low-Temperature Microstructure	215
8.4	Theoretical Model of Twin Boundary Structure	224
8.4.1	Landau Model	225
8.4.2	The Structure of Twin Boundary	227
8.4.3	The Size of the Twin Domains	233
8.5	Summary	236
9	Kinetics of the Alignment and the Formation of Bi-2223	237
9.1	Introduction	237

9.2	The Fabrication Procedure	241
9.3	Evolution at Early Stages of Heat Treatment	244
9.3.1	<i>In situ</i> X-ray Diffraction Measurements	245
9.3.2	Electron Microscopy	248
9.3.3	The Formation of Bi-2223	262
9.4	Dislocation and Bismuth 2212-to-2223 Transformation	271
9.4.1	Introduction	271
9.4.2	Edge-dislocations as Channels for Fast Ion Diffusion	274
9.4.3	The Layer Rigidity Model	275
9.4.4	Kinetics of Bi-2212 Conversion to Bi-2223	282
9.5	Summary	287
10	Charge Distribution	289
10.1	Introduction	289
10.2	Bi ₂ Sr ₂ CaCu ₂ O ₈	292
10.2.1	A General Nano-scale Description	292
10.2.2	Direct Imaging of Charge Modulation	295
10.3	YBa ₂ Cu ₃ O ₇	301
10.3.1	A Novel Diffraction Method	301
10.3.2	Distribution of Electron Holes	308
10.4	Conclusion	312
11	Experimental Techniques for Grain Boundary Studies	313
11.1	Analyses of Grain Boundary Crystallography	314
11.1.1	Determination of Grain Boundary Geometry	314
11.1.2	Case Study of YBa ₂ Cu ₃ O _{7-δ}	320
11.2	Electron Energy-Loss Spectroscopy of Oxygen K-edge	328
11.2.1	Experimental Considerations of TEM-EELS	329
11.2.2	Orientational Dependence of the Oxygen Pre-peak	334
11.2.3	Quantitative Analysis of Oxygen/hole Concentration	337
11.3	Lattice Parameter from CBED Measurement of HOLZ Pattern	340

12 The Structure of Grain Boundaries	345
12.1 Introduction	345
12.2 Grain Boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	346
12.2.1 Misorientation Distribution in Textured Bulks	347
12.2.2 Grain Boundary Dislocations	352
12.2.3 Oxygen Content and CCSL Boundaries	355
12.2.4 Variation of Oxygen/hole at the Boundaries	358
12.2.5 Cation Segregation at the Boundary	368
12.2.6 Strain Energy of the Grain Boundaries	371
12.3 Grain Boundaries in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$	376
12.3.1 Misorientation Distribution in Bi-2212 and Bi-2223 Composite Tapes	378
12.3.2 Superconducting Properties of Twist Boundaries of Bi-2212	383
12.3.3 Structural Features of the Twist Boundaries	387
12.4 RSJ Model	403
12.5 Summary	417
13 Artificially Created Defects	419
13.1 Introduction	419
13.2 Experimental Methods	420
13.2.1 Sample Preparation	420
13.2.2 Heavy-ion Irradiation	421
13.3 Structure of the Defects	421
13.3.1 General Morphology	421
13.3.2 Radiation Damage Induced by Au, Ag, Cu, and Si Ions	424
13.3.3 The Effect of Crystallographic Orientation	430
13.3.4 The Effects of Oxygen Concentration in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	431
13.3.5 The Effect of the Pre-existing Crystal Imperfections	435
13.3.6 Creation of Stacking Faults	437
13.3.7 EELS Measurements	439
13.4 Thermal Spike Model	441
13.4.1 Stopping Power of Heavy Ions	442
13.4.2 The Size of the Defect Area	443
13.4.3 Anisotropy of the Size and Shape of the Defects	448

13.5 Strain Field and Strain Contrast of Columnar Defects . .	450
13.5.1 The Displacement Fields of Columnar Defects . .	451
13.5.2 Intensity of the Diffraction Contrast of the Columnar Defects	455
13.5.3 Simulation of the Strain Contrast of the Colum- nar Defects	457
13.5.4 The Radial Displacement and Strain of the Columnar Defects	462
13.6 Planar Defects Induced by Heavy-ion Irradiation	465
13.6.1 Morphology of the Planar Defects	465
13.6.2 Microchemical Analysis of the Planar Defects . .	467
13.6.3 Structure of the Planar Defects	469
13.7 Summary	474
14 Conclusions	477
Bibliography	479
Index	505