Physics and Chemistry of Low-Dimensional Inorganic Conductors

NATO ASI Series

Advanced Science Institutes Series

A series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation
B Physics	New York and London
C Mathematical and Physical Sciences	Kluwer Academic Publishers
D Behavioral and Social Sciences	Dordrecht, Boston, and London
E Applied Sciences	
F Computer and Systems Sciences	Springer-Verlag
G Ecological Sciences	Berlin, Heidelberg, New York, London,
H Cell Biology	Paris, Tokyo, Hong Kong, and Barcelona
I Global Environmental Change	

PARTNERSHIP SUB-SERIES

1. Disarmament Technologies	Kluwer Academic Publishers
2. Environment	Springer-Verlag
3. High Technology	Kluwer Academic Publishers
4. Science and Technology Policy	Kluwer Academic Publishers
5. Computer Networking	Kluwer Academic Publishers

The Partnership Sub-Series incorporates activities undertaken in collaboration with NATO's Cooperation Partners, the countries of the CIS and Central and Eastern Europe, in Priority Areas of concern to those countries.

Recent Volumes in this Series:

Volume 352—History of Original Ideas and Basic Discoveries in Particle Physics
edited by Harvey B. Newman and Thomas Ypsilantis

Volume 353—Hadron Spectroscopy and the Confinement Problem
edited by D. V. Bugg

Volume 354—Physics and Chemistry of Low-Dimensional Inorganic Conductors
edited by Claire Schlenker, Jean Dumas, Martha Greenblatt,
and Sander van Smaalen

Volume 355—Stability of Materials
edited by A. Gonis, P. E. A. Turchi, and Josef Kudrnovsky

Series B: Physics

Physics and Chemistry of Low-Dimensional Inorganic Conductors

Edited by

Claire Schlenker

CNRS and Institut National Polytechnique de Grenoble
Grenoble, France

Jean Dumas

CNRS
Grenoble, France

Martha Greenblatt

Rutgers, The State University of New Jersey
Piscataway, New Jersey

and

Sander van Smaalen

University of Bayreuth
Bayreuth, Germany

Plenum Press

New York and London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of a NATO Advanced Study Institute on
Physics and Chemistry of Low-Dimensional Inorganic Conductors,
held June 13 – 23, 1995,
in Les Houches, France

NATO-PCO-DATA BASE

The electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to about 50,000 contributions from international scientists published in all sections of the NATO ASI Series. Access to the NATO-PCO-DATA BASE is possible in two ways:

—via online FILE 128 (NATO-PCO-DATA BASE) hosted by ESRIN, Via Galileo Galilei, I-00044 Frascati, Italy

—via CD-ROM "NATO Science and Technology Disk" with user-friendly retrieval software in English, French, and German (©WTV GmbH and DATAWARE Technologies, Inc. 1989). The CD-ROM contains the AGARD Aerospace Database.

The CD-ROM can be ordered through any member of the Board of Publishers or through NATO-PCO, Overijse, Belgium.

Library of Congress Cataloging-in-Publication Data

Physics and chemistry of low-dimensional inorganic conductors / edited
by Claire Schlenker ... [et al.].

p. cm. -- (NATO ASI series. B, Physics ; v. 354)

"Proceedings of a NATO Advanced Study Institute on Physics and
Chemistry of Low-Dimensional Inorganic Conductors, held June 13-23,
1995, in Les Houches, France"---T.p. verso.

"Published in cooperation with NATO Scientific Affairs Division."

Includes bibliographical references and index.

ISBN-13: 978-1-4612-8449-9

e-ISBN-13: 978-1-4613-1149-2

DOI: 10.1007/978-1-4613-1149-2

1. One-dimensional conductors--Congresses. 2. Charge density
waves--Congresses. I. Schlenker, Claire, 1940- . II. North
Atlantic Treaty Organization. Scientific Affairs Division.
III. NATO Advanced Study Institute on Physics and Chemistry of Low
-Dimensional Inorganic Conductors (1995 : Les Houches, France)
IV. Series.

QC176.B.E4P547 1996

537.6'2--dc20

96-17037
CIP

© 1996 Plenum Press, New York

Softcover reprint of the hardcover 1st edition 1996

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N. Y. 10013

10 9 8 7 6 5 4 3 2 1

All rights 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, microfilming, recording, or otherwise, without written permission from the Publisher

PREFACE

The field of low-dimensional conductors has been very active for more than twenty years. It has grown continuously and both the inorganic and organic materials have remarkable properties, such as charge and spin density waves and superconductivity. The discovery of superconductivity at high temperature in copper-based quasi two-dimensional conducting oxides nearly ten years ago has further enlarged the field and stimulated new research on inorganic conductors. It was obviously impossible to cover such a broad field in a ten day Institute and it seemed pertinent to concentrate on inorganic conductors, excluding the high T_c superconducting oxides. In this context, it was highly desirable to include both physics and chemistry in the same Institute in order to tighten or in some cases to establish links between physicists and chemists.

This Advanced Study Institute is the continuation of a series of similar ones which have taken place every few years since 1974. 73 participants coming from 13 countries have taken part in this School at the beautiful site of the Centre de Physique des Houches in the Mont-Blanc mountain range. The scientific programme included more than forty lectures and seminars, two poster sessions and ten short talks. Several discussion sessions were organized for the evenings, one on New Materials, one on New Topics and one on the special problem of the Fermi and Luttinger liquids. The scientific activity was kept high from the beginning to the end of the Institute.

The Institute was focused on the chemical aspects and the physical properties of families of transition metal oxides, chalcogenides and bronzes showing quasi one-dimensional or two-dimensional electronic properties.

A general introduction to low-dimensional inorganic conductors was given from the chemist's point of view, with emphasis on the chalcogenide families, including the quasi two-dimensional transition metal dichalcogenides and quasi one-dimensional trichalcogenides such as NbSe_3 , and tetrachalcocogenides. The molybdenum and tungsten bronzes, such as the quasi one-dimensional blue bronze $\text{K}_{0.30}\text{MoO}_3$, the quasi two dimensional purple bronze $\text{KMo}_6\text{O}_{17}$ and the new series of the monophosphate tungsten bronzes $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ were extensively discussed. Other families of compounds were presented, which may attract the interest of physicists in the near future. These include the ternary cluster compounds of molybdenum, the misfit layered chalcogenides and new layered chalcogenides obtained by synthesis at intermediate temperatures. The nature and the role of defects, as studied by electron microscopy, were described for some oxides and bronze families.

Lectures on the physical properties were focused on the charge density wave instabilities and related properties. Detailed studies of the high temperature "normal" state by techniques such as electron spectroscopies were discussed in relation with band structure calculations and possible Luttinger liquid properties in quasi one-dimensional conductors. The role of fluctuations in quasi one-dimensional systems was emphasized. The properties

of the phase transitions leading to the charge density wave states were described especially in relation to the structural aspects. In the low temperature charge density wave (CDW) state, the nature of excitations was discussed. The electrodynamics of density waves including their optical properties were extensively presented. Several lectures were devoted to the non linear transport properties due to the depinning of the CDW. The role of CDW defects, such as CDW dislocations (phase slip centers) was recognized by all. Time resolved and spatially resolved studies using x-ray synchrotron radiation support this view. Local techniques provided by scanning tunneling microscopy and atomic force microscopy might corroborate this in the near future. Finally, new directions were given by the Lectures on Wigner crystals and the possibility of Wigner crystallization in low-dimensional inorganic conductors was discussed.

Thanks are due to all lecturers and participants for the success of the Institute, which could not have taken place without the sponsoring of NATO and CNRS (Formation Permanente). The scientific advice of J.P. Pouget has been appreciated on several occasions. Financial support was obtained from Ministère des Affaires Etrangères and Ministère de la Défense (DGA-DRET). We would like to thank the Director and Staff of the Centre de Physique des Houches, connected to the Université Joseph Fourier and Institut National Polytechnique de Grenoble and subsidized by Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche, Centre National de la Recherche Scientifique and Commissariat à l'Energie Atomique. Administrative and technical help from P. Caillat-Miousse, K. Guibreteau and C. Hess is acknowledged.

Claire Schlenker
Jean Dumas
Martha Greenblatt
Sander van Smaalen

PREFACE

Depuis plus de vingt ans, le domaine des conducteurs de basse dimensionnalité a été très vivant. Il s'est développé régulièrement et les matériaux inorganiques ainsi qu'organiques présentent des propriétés remarquables, telles que celles d'ondes de densité de charge et de spin et de supraconductivité. La découverte de la supraconductivité à haute température dans des oxydes conducteurs quasi-bidimensionnels à base de cuivre il y a près de dix ans a élargi le domaine et a stimulé de nouvelles recherches sur les conducteurs inorganiques. Il était évidemment impossible de couvrir un aussi large domaine pendant un Institut de dix jours et il semblait opportun de se limiter aux conducteurs inorganiques en excluant les oxydes supraconducteurs à haute température. Dans ce contexte, il était très souhaitable d'inclure à la fois la physique et la chimie dans le même Institut de manière à renforcer ou, dans certains cas, à établir des liens entre physiciens et chimistes.

Cet Institut d'Etudes Avancées est la suite d'une série d'Instituts semblables qui ont eu lieu tous les deux ou trois ans depuis 1974. 73 participants provenant de 13 pays ont pris part à cette Ecole dans le magnifique site du Centre de Physique des Houches, dans la chaîne du Mont Blanc. Le programme scientifique comportait plus de quarante cours et séminaires, deux séances d'affiches et dix brefs exposés. Plusieurs sessions consacrées à des discussions furent organisées en soirée, une sur les Nouveaux Matériaux, une sur de Nouveaux Sujets et une autre sur le problème particulier des liquides de Fermi et de Luttinger. Le niveau de l'activité scientifique resta très haut d'un bout à l'autre de l'Institut.

L'Institut fut consacré aux aspects chimiques et aux propriétés physiques de familles d'oxydes de métaux de transition, chalcogénures et bronzes présentant des propriétés électroniques quasi unidimensionnelles ou quasi bidimensionnelles.

Une introduction générale aux conducteurs de basse dimensionnalité fut donnée du point de vue du chimiste, avec une attention particulière pour les familles de chalcogénures, incluant les dichalcogénures bidimensionnels de métaux de transition et les trichalcogénures quasi unidimensionnels tels que NbSe_3 , et les tétrachalcogénures. Les bronzes de tungstène et de molybdène, tels que le bronze bleu quasi unidimensionnel $\text{K}_{0.30}\text{MoO}_3$, le bronze violet quasi bidimensionnel KM_6O_{17} et la nouvelle série de bronzes monophosphatés de tungstène $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ furent discutés en détail. D'autres familles de composés furent présentées, qui peuvent attirer l'attention des physiciens dans un proche avenir. Celles-ci comprennent les composés ternaires de molybdène à amas, les chalcogénures à couches alternées et de nouveaux chalcogénures lamellaires obtenus par synthèse à des températures modérées. La nature et le rôle des défauts, étudiés notamment par microscopie électronique, furent décrits dans le cas de quelques oxydes et bronzes.

Les cours sur les propriétés physiques furent centrés sur les instabilités d'onde de densité de charge et les propriétés qui leur sont attachées. Des études détaillées sur l'état "normal" haute température par des techniques telles que les spectroscopies d'électrons

furent discutées en relation avec les calculs de structure de bandes et les propriétés possibles de liquide de Luttinger dans les conducteurs quasi unidimensionnels. Le rôle des fluctuations dans les systèmes quasi unidimensionnels fut souligné. Les propriétés des transitions de phases conduisant à des états à onde de densité de charge furent décrites tout particulièrement en liaison avec les aspects structuraux. La nature des excitations dans l'état à onde de densité de charge à basse température, a été discutée. L'électrodynamique des ondes de densité, incluant leurs propriétés optiques, fut présentée en détail. Plusieurs cours furent consacrés aux propriétés de transport non linéaire dues au dépiégeage des ondes de densité de charge. Le rôle des défauts d'onde de densité de charge, tels que les dislocations (centres de glissement de la phase) fut admis par tous. Des expériences résolues en temps et dans l'espace, faisant appel au rayonnement synchrotron, sont en accord avec ce point de vue, que des techniques locales telles que la microscopie tunnel et à force atomique pourraient corroborer dans un proche avenir. Enfin, de nouvelles perspectives furent apportées par des conférences sur les cristaux de Wigner et la possibilité de cristallisation de Wigner dans des conducteurs inorganiques de basse dimensionnalité fut discutée.

Nos remerciements vont à tous les conférenciers et participants pour le succès de cet Institut, qui n'aurait pu avoir eu lieu sans l'aide financière de l'OTAN et du CNRS (Formation Permanente). A plusieurs occasions, nous avons pu apprécier les conseils scientifiques de J.P. Pouget. Le Ministère des Affaires Etrangères et le Ministère de la Défense (DGA-DRET) ont fourni une aide financière. Nous remercions le Directeur et le personnel du Centre de Physique des Houches, rattaché à l'Université Joseph Fourier et à l'Institut National Polytechnique de Grenoble et financé par le Ministère de l'Education Nationale, de l'Enseignement Supérieur, de la Recherche, le Centre National de la Recherche Scientifique et le Commissariat à l'Energie Atomique. Nous remercions P. Caillat-Miousse, K. Guibreteau et C. Hess pour leur aide administrative et technique.

Claire Schlenker
Jean Dumas
Martha Greenblatt
Sander van Smaalen

CONTENTS

MATERIALS AND CHEMISTRY

1. An Introduction to the Design of Low-Dimensional Solids 1
J. Rouxel
2. Molybdenum and Tungsten Bronzes: Low-Dimensional Metals with Unusual
Properties 15
M. Greenblatt
3. Nanostructures of Low Dimensional Oxides: Nature and Role of Defects 45
M. Hervieu
4. Misfit Layer Compounds $(MX)_{1+x}(TX_2)_m$ M= Pb, Bi, Sn; T = Ti, V, Cr, Ta, Nb;
X = S, Se; $0.08 < x < 0.28$; m = 1, 2, 3 59
J. Rouxel and A. Meerschaut
5. Clusters in Reduced Molybdenum and Tungsten Oxide and Sulfide Systems 71
R. E. McCarley
6. New Materials from Reactions in Intermediate Temperature Molten Salts.
Synthetic Methodologies for Multinary Solid State Chalcogenides 83
M. G. Kanatzidis

INTRODUCTION TO CHARGE DENSITY WAVES, SPIN DENSITY WAVES AND WIGNER CRYSTALS

7. Density Waves in Linear Chain Compounds 101
G. Grüner
8. Charge Density Waves in Quasi Two-Dimensional Inorganic Conductors -
Molybdenum and Phosphate Tungsten Bronzes 115
C. Schlenker
9. Organic Superconductors and Spin Density Waves 141
D. Jérôme

10. Wigner Crystals 171
P. B. Littlewood, A. J. Millis, and X. J. Zhu

STRUCTURAL STUDIES

11. Structural and Dynamical Aspects of the Charge Density Wave Instability 185
J. P. Pouget
12. Incommensurately Modulated Structures of Inorganic Charge Density Wave
Compounds 219
S. van Smaalen
13. Scanning Tunneling Microscopy and Atomic Force Microscopy on Charge
Density Wave and Related Materials 229
R. Wiesendanger
14. Interpreting Scanning Tunneling and Atomic Force Microscopy Images 241
M. -H. Whangbo, J. Ren, S. N. Magonov, and H. Bengel

ELECTRONIC STRUCTURES: THEORY AND EXPERIMENT

15. The Electronic Structure of Transition Metal Oxides and Chalcogenides 255
P. A. Cox
16. Fermi Surface Nesting and Electronic Instabilities in Transition Metal Oxides
and Bronzes 271
E. Canadell and M. -H. Whangbo
17. Structural and Electronic Instabilities of Transition Metal Chalcogenides 285
M. -H. Whangbo, D. -K. Seo, and E. Canadell
18. Photoemission Studies in Transition Metal Oxides and Chalcogenides 303
D. Malterre, M. Grioni, and Y. Baer
19. Angle Resolved Photoemission and Resonant Photoemission Studies of Quasi
Low-Dimensional Oxide Conductors: Fermi Surfaces and Defects 313
K. E. Smith, K. Breuer, C. Stagescu, M. Greenblatt, W. McCarroll, and
K. Ramanujachary
20. Fermi and Luttinger Liquids in Low-Dimensional Metals 327
C. Castellani and C. Di Castro

THERMAL PROPERTIES AND EXCITATIONS

21. Thermal Lattice Fluctuations in Quasi One-Dimensional Conductors: Optical
Experiments 337
L. Degiorgi, St. Thieme, B. Alavi, G. Grüner, R. H. McKenzie, K. Kim, and
F. Lévy

22. Elastic and Thermal Properties of Low-Dimensional Conductors 345
J. W. Brill
23. Glassy Behaviour and Metastability in the Charge or Spin Density Wave State .. 357
K. Biljakovic

DYNAMICS OF CHARGE AND SPIN DENSITY WAVES: NON LINEAR TRANSPORT, DISLOCATIONS AND PLASTICITY

24. Introduction to Charge Density Wave Transport: Basic Phenomena and Models 371
P. Monceau
25. Theory of Charge and Spin Density Wave Transport 389
W. Wonneberger
26. Dislocations in the Charge Density Wave State of NbSe₃ : I Phase Slip
Properties 411
J. C. Gill
27. Dislocations in the Charge Density Wave State of NbSe₃: II Bulk Charge
Density Wave Transport 421
J. C. Gill
28. Charge Density Wave Dynamics in the Blue Bronzes A_{0.30}MoO₃ (A=K, Rb) 431
J. Dumas
29. Photoinduced Properties of Charge Density Wave Materials 443
G. Mihaly
30. Spatially-Resolved Studies of Charge Density Wave Deformations and Phase
Slip in NbSe₃ 453
T. L. Adelman, D. A. DiCarlo, M. C. de Lind van Wijngaarden,
M. P. Maher, J. D. Brock, and R. E. Thorne
31. Intrinsic Defects and Plasticity in Charge and Spin Density Waves 465
S. Brazovskii
- Participants Photo 475
- Index 479