

Chemical
Bonding
and
Spectroscopy
in
Mineral
Chemistry

Chemical
Bonding
and
Spectroscopy
in
Mineral
Chemistry

EDITED BY

Frank J. Berry

*Department of Chemistry
University of Birmingham, UK*

and

David J. Vaughan

*Department of Geological Sciences
University of Aston in Birmingham, UK*

London New York
CHAPMAN AND HALL

First published 1985 by
Chapman and Hall Ltd
11 New Fetter Lane, London EC4P 4EE

Published in the USA by
Chapman and Hall
733 Third Avenue, New York NY 10017

© 1985 Chapman and Hall Ltd
Softcover reprint of the hardcover 1st edition 1985

ISBN-13: 978-94-010-8645-5 e-ISBN-13: 978-94-009-4838-9
DOI: 10.1007/978-94-009-4838-9

*All rights reserved. No part of this book may be
reprinted, or reproduced or utilized in any form or by
any electronic, mechanical or other means, now known
or hereafter invented, including photocopying and
recording, or in any information storage and retrieval
system, without permission in writing from the publisher.*

British Library Cataloguing in Publication Data

Chemical bonding.

1. Mineralogical chemistry
 2. Chemical bonds 2. Spectrum analysis
- I. Berry, Frank J. II. Vaughan, David J.
549'.133 QE371

Library of Congress Cataloging in Publication Data

Main entry under title:

Chemical bonding and spectroscopy in mineral chemistry.

Includes bibliographies and index.

1. Mineralogical chemistry. 2. Chemical bonds.
 3. Spectrum analysis. I. Berry, Frank J., 1947–
II. Vaughan, David J., 1946–
QE371.C46 1984 549'.13 84-15542
-

Contents

Contributors	viii
Preface	ix
1 Quantum Mechanical Models and Methods in Mineralogy	1
J.A. Tossell	
1.1 Introduction	1
1.2 Full lattice calculations	5
1.3 Cluster calculations on mineral structural properties	6
1.4 Cluster calculations on mineral spectral properties	14
1.5 Cluster calculations of valence electron density distributions	19
1.6 Applications of qualitative MO theory	22
1.7 Conclusions	26
Acknowledgements	27
References	28
2 X-ray Spectroscopy and Chemical Bonding in Minerals	31
D.S. Urch	
2.1 Introduction	31
2.2 Photoelectron and X-ray spectroscopy	32
2.3 Spectroscopic techniques	36
2.4 Application of XES and XPS to bonding studies in mineral chemistry	42
2.5 Further developments	57
2.6 Conclusions	59
References	59
3 Electronic Spectra of Minerals	63
Roger G. Burns	
3.1 Introduction	63

3.2 Background	64
3.3 Techniques	72
3.4 Crystal field spectra	74
3.5 Intervalence transitions	86
3.6 Applications	89
3.7 Summary	98
References	99
4 Mineralogical Applications of Luminescence Techniques	103
Grahame Walker	
4.1 Introduction	103
4.2 The luminescence process	104
4.3 Experimental techniques	121
4.4 Luminescence centres in some common minerals	126
4.5 Some conclusions	136
References	138
5 Mössbauer Spectroscopy in Mineral Chemistry	141
A.G. Maddock	
5.1 The basis of Mössbauer spectroscopy	141
5.2 The hyperfine interactions	143
5.3 The Mössbauer factor, f , and the intensity of the absorption lines	153
5.4 ^{57}Fe Mössbauer parameters and deductions from such data	155
5.5 Experimental details	162
5.6 Mineralogical applications	168
5.7 Antimony	191
5.8 Other physical studies	191
References	191
6 Electron Spin Resonance and Nuclear Magnetic Resonance Applied to Minerals	209
William R. McWhinnie	
6.1 Electron spin resonance spectroscopy	210
6.2 Practical aspects of ESR	216
6.3 Some applications of ESR in mineral chemistry	219
6.4 Nuclear magnetic resonance spectroscopy	227
6.5 NMR of solids	231
6.6 Applications	235
6.7 High resolution NMR studies of minerals	237
6.8 Conclusion	246
Acknowledgement	246
References	246

7 Spectroscopy and Chemical Bonding in the Opaque Minerals	251
David J. Vaughan	
7.1 Introduction	251
7.2 Compositions and crystal structures of the major opaque minerals	252
7.3 Approaches to chemical bonding models	255
7.4 Experimental methods for the study of bonding	257
7.5 Chemical bonding in some major opaque mineral groups	260
7.6 Concluding remarks	289
References	290
8 Mineral Surfaces and the Chemical Bond	293
Frank J. Berry	
8.1 Introduction	293
8.2 Spectroscopic techniques	293
8.3 Applications in mineral chemistry	301
8.4 Concluding remarks	313
References	313
Index	316

Contributors

F.J. Berry

Department of Chemistry, University of Birmingham, Birmingham, UK.

R.G. Burns

Department of Earth, Atmosphere and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA.

A.G. Maddock

University Chemical Laboratory, Cambridge, UK.

W.R. McWhinnie

Department of Chemistry, University of Aston in Birmingham, Birmingham, UK.

J.A. Tossell

Department of Chemistry, University of Maryland, College Park, MD, USA.

D.S. Urch

Department of Chemistry, Queen Mary College, University of London, London, UK.

D.J. Vaughan

Department of Geological Sciences, University of Aston in Birmingham, Birmingham, UK.

G. Walker

Department of Pure and Applied Physics, UMIST, Manchester, UK.

Preface

In recent years mineralogy has developed even stronger links with solid-state chemistry and physics and these developments have been accompanied by a trend towards further quantification in the theoretical as well as the experimental aspects of the subject.

The importance of solid-state chemistry to mineralogy was reflected in a symposium held at the 1982 Annual Congress of The Royal Society of Chemistry at which the original versions of most of the contributions to this book were presented. The meeting brought together chemists, geologists and mineralogists all of whom were interested in the application of modern spectroscopic techniques to the study of bonding in minerals. The interdisciplinary nature of the symposium enabled a beneficial exchange of information from the various fields and it was felt that a book presenting reviews of the key areas of the subject would be a useful addition to both the chemical and mineralogical literature.

The field of study which is commonly termed the 'physics and chemistry of minerals' has itself developed very rapidly over recent years. Such rapid development has resulted in many chemists, geologists, geochemists and mineralogists being less familiar than they might wish with the techniques currently available. Central to this field is an understanding of chemical bonding or 'electronic structure' in minerals which has been developed both theoretically and by the use of spectroscopic techniques. The purpose of this book is to outline the fundamental concepts associated with current models of bonding and to serve as an introduction to the techniques which may be applied in this area of mineral chemistry. It is not the intention of the text to provide a laboratory manual for the techniques discussed, neither is it intended that reviews of the literature detailing applications be comprehensive. This book is a starting point from which the interested reader can progress to many of the more detailed accounts cited in the various chapters.

The book begins with a chapter on the use of quantum mechanics in producing models of chemical bonding in minerals. The next two chapters

consider the application of X-ray spectroscopy and of electronic absorption spectroscopy and are followed by a chapter on the more specialist technique of luminescence spectroscopy. All of these methods involve the interaction of some form of electromagnetic radiation with the electrons in solids and provide information about the energies and distributions of the electrons. The next two chapters deal largely with the interaction of radiation with atomic nuclei in minerals as in Mössbauer spectroscopy and nuclear magnetic resonance. These techniques generally serve as more indirect, although equally powerful, probes of the electronic structures of solids. The last two chapters deal with the special problems, as regards both theory and experiment, which are posed by opaque minerals and with the applications of spectroscopic methods for the elucidation of the surface properties of minerals.

If the readers of this book are consequently led to look more deeply into the fascinating areas of bonding and spectroscopy in mineral chemistry then our objectives will have been achieved.

F.J. Berry
D.J. Vaughan
Birmingham, 1984