

Physics and Chemistry of Electrons and Ions in Condensed Matter

edited by

J. V. Acrivos

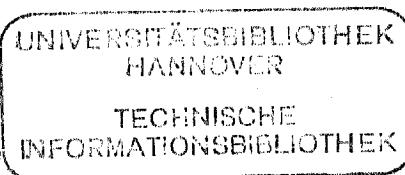
San José University, San José, California, U.S.A. and
Trinity College, Cambridge, U.K.

N. F. Mott

Cavendish Laboratory, Cambridge, U.K. and
Gonville and Caius College, Cambridge, U.K.

A. D. Yoffe

Cavendish Laboratory, Cambridge, U.K. and
Darwin College, Cambridge, U.K.



D. Reidel Publishing Company

Dordrecht / Boston / Lancaster

Published in cooperation with NATO Scientific Affairs Division

CONTENTS

Preface

xvii

PART I

PROPERTIES OF CRYSTALLINE MATERIALS

The Effective U in Oxides and in Sulfides: Conceptual Phase	
Diagrams and their Applications	1
John B. Goodenough	
1. Definitions	1
2. Interatomic interactions	23
References	44
Electron Correlations in Elementary Structures. The Case of Weak Correlations : Metallic and Covalent Bondings	45
J. Friedel	
Introduction	45
1. The H ₂ molecule	46
2. Other elementary diatomic molecules	52
3. Metallic aggregates	53
4. Macroscopic phases of transition metals	57
5. Aggregates and solids of tetravalent (sp) elements	64
6. Aggregates of covalent dimers	67
7. Weak distortions of metallic closepacked or covalent structures	69
Appendixes	74
References	82
Statistical Thermodynamics of Mixed Valence at Low Temperatures.....	85
Dieter Wohleben	
1. Introduction	85
2. The free enthalpy without mixing	86
3. The valence fluctuation temperature	89
4. The free enthalpy with interconfigurational mixing	90
5. Equation of state for the valence fluctuation temperature	94
6. The conduction electron density of states near T=0	98
7. Application to Ce metal	101
8. Acknowledgements	104
References	104
Mixed Valency in Inorganic Chemistry.....	109
P. Day	

Important Discussion of Part I

Intermediate Valency (IV) Compounds 111
N. F. Mott

Thermal Expansion and Specific Heat of Mixed Valence
Compounds 117
R. Pott
 1. Introduction 117
 2. Experiments and experimental results 117
 3. Discussion 120
 4. Acknowledgements 122
 5. References 122

The Contribution of Solid State Chemistry to Diversification of
the Studies on Metal-Insulator Transition 123
J. P. Doumerc

The Study of Metal to Non-Metal Transitions by High Resolution
Electron Spectroscopy 129
R. G. Egdell

Electrical Properties of Rutile Type Oxides : Doped TiO_2 and
 RuO_2 130
P. Triggs and F. Levy

Mixed Anion Valencies in Copper Sulfides and Selenides 131
F. Jellinek

Charge Transfer and Exciton Satellites in the Photoelectron
Spectra of Transition Metal Compounds 132
C. Haas

Direct Determination of Electron Correlation in a Simple
Binuclear Complex 133
C. Haas

Hall Effect in Vitreous 80 V_2O_5 - 20 P_2O_5 134
A. Vomvas and R. Roilos

Application of Group Theory to X-Ray Absorption Edge Studies .. 135
B. McQuillan

On Discrete Symmetry Groups for Systems with an Odd Number of Electrons.....	143
H. P. Fritzer	

Superconductivity in the BaPb _{1-x} BixO ₃ System.....	144
M. L. Norton	

PART II

PROPERTIES OF AMORPHOUS SOLIDS AND LIQUIDS

Electronic Properties of Non-Crystalline Semiconductors.....	145
--	-----

E. A. Davis	
1. Introduction	145
2. Structure	146
3. Densities of states and optical properties	148
4. Localized states and mobility edges	149
5. Point defects	151
6. Time-of-flight experiments	153
7. Densities of states in the gap	160
8. Luminescence	161
9. Conclusions	163
References	163

Thermodynamics of Condensed Ionic Systems.....	165
--	-----

K. S. Pitzer	
1. Introduction	165
2. Screening of interionic forces	167
3. Mixtures with forces screened to short range	174
4. Miscible fused salt - Molecular liquid systems	178
5. Strong unscreened electrical forces	184
References	194

Transport Properties at the Metal-Insulator Transition in Metal Ammonia Solutions.....	197
--	-----

J. C. Thompson.	
1. Experimental results	197
2. Analysis	204
3. Acknowledgement	207
4. References	207

Electrons and Ions in Liquid and Amorphous Metals.....	211
--	-----

H.-J. Güntherodt	
------------------	--

1. Introduction	211
2. Atomic scale structure	213
3. Dynamical properties	217
4. Electronic structure	220
5. Electronic transport	224
6. Conclusion	227
Acknowledgements	227
References	227
Molten Salts and Liquid Semiconductors : Structure and Electrical Properties.....	231
J. E. Enderby	
1. Introduction	231
2. Liquid semiconductors based on Tellurium	233
3. The method of neutron diffraction with isotopic substitution	237
4. Future prospects	252
References	253
Structure-Transport Relations in Molten Salts.....	255
K. G. Weil	
1. Introduction	255
2. Alkali Halides	256
3. Silver Halides	262
Appendix	269
Acknowledgement	269
References	269
<u>Important Discussion of Part II</u>	
EXAFS Study of the Structure of Molten CuCl.....	273
J. B. Boyce and J. C. Mikkelsen, Jr.	
Bonding at Bulk and Defect Sites in Amorphous Semiconductors..	279
J. Robertson	
Regular Rings in Glasses.....	283
F. L. Galeener	
Size Effects in Semiconductors.....	284
J. J. Ramsden	

Photoinduced Changes in Amorphous Chalcogens.....	285
R. T. Phillips	

PART III

METAL TO INSULATOR TRANSITIONS

Metal Insulator Transitions.....	287
N. F. Mott	

Magnetism and Magnetic Resonance Across the Metal-Nonmetal Transition.....	297
---	-----

Peter P. Edwards	
1. Preamble	297
2. The metal-nonmetal transition: global considerations	301
3. A survey of magnetic properties: microscopic considerations	306
4. Concluding remarks	327
Acknowledgements	328
References	329

X-ray Absorption Spectroscopy across the Metal to Non-metal Transition.....	335
--	-----

J. V. Acrivos	
1. Introduction	335
2. Solvation across the metal to insulator transition	337
3. Structure and thermodynamic relations	342
4. Discussion	349
References	351
Appendix with Applications	353

Thermodynamics and Electrochemistry of Sodium-Ammonia Solutions and of Solvated Electrons in Ammonia.....	361
--	-----

U. Schindewolf	
1. Introduction	361
2. Thermodynamics of sodium ammonia solutions	363
3. Thermodynamics of solvated electrons in ammonia	366
4. Absolute electrode potentials	368
5. Electrode potential determining particle	370
6. Thermodynamics of solvated electrons in water	372
7. A new phase instability in sodium ammonia solutions	373
8. Solid $\text{Na}(\text{NH}_3)_3$ - An expanded metal	375
9. Delocalized and localized electrons in polar vapors	377
10. Lithium isotope separations	378
References	380

Solvated Electrons.....	385
J. C. Thompson	
1. Introduction	385
2. Basic observations	386
3. Theory	389
4. Further observations	392
5. Final remarks	397
6. Acknowledgements	398
7. References	398
Phase Separation in Expanded Metallic Liquids.....	401
F. Hensel	
1. Introduction	401
2. The critical point of pure metals	403
3. Metallic solutions near the critical point of an almost pure solvent	420
References	423

Important Discussion of Part III

The Properties of Doped Liquid Iodine Melts.....	427
J. Kommandeur	

Low Frequency Dielectric Constant and Electrical Conductivity of Dense Mercury Vapour.....	429
G. Schönherr	

Transport Properties of Chloride and Fluoride Glass-Forming Melts, Its Relationship with Coordination Numbers.....	435
A. M. Elias, C. Esp. de Massa, C. I. 1	

PART IV

LOW DIMENSIONAL MATERIALS (LDS)

IV-I Two Dimensional - LDS

Electronic Properties of Intercalate Complexes of Layer Type Transition Metal Dichalcogenides.....	437
A. D. Yoffe	
1. Introduction	437

2. Intercalation with organic molecules and related compounds	442
3. Intercalation with alkali metal atoms	444
4. Intercalation with "3d" transition metals	451
5. Practical applications	454
References	457
Band Structure and Optical Properties of Layer Compounds.....459	
W. Y. Liang	
1. Introduction	459
2. The atomic orbital approach	461
3. Consequence of the trigonal distortion	463
4. Anisotropy in transport properties	467
5. Fermi surface nesting and charge density waves	470
6. Optical properties	470
7. Conclusion	475
References	476
LDS Intercalation with Donor and Acceptor Molecules.....479	
J. V. Acrivos	
1. Introduction	479
2. Analysis of results	481
3. Discussion of results	491
4. Future and application of intercalation studies	492
5. Physical significance and possible extensions of this work	492
Bibliography	495
Appendix: Phase Transitions Produced by Intercalation	505
Physico-Chemical Aspects of Intercalation Phenomena.....521	
J. M. Thomas	
1. Introduction	522
2. Graphite intercalates	522
3. Sheet silicates	529
4. $\text{Na}_x(\text{x}-1)^+$ species intercalated with zeolitic hosts	535
5. WO_3 -based hosts	538
6. New techniques	540
References	542
<u>Important Discussion of Part IV-I</u>	
Ag Intercalation of TiS_2545	
R. F. Frindt	

Transport and Raman Investigation of the Group IV Layered Compounds and their Lithium Intercalates.....	549
P. C. Klipstein, C. M. Pereira and R. H. Friend	
1. Introduction	549
2. Experimental details	551
3. Transport properties	552
4. Discussion	556
5. Raman investigation	557
6. Conclusions	558
References	559
Ion-Electron Interaction and Intercalation Induced Semiconductor to Metal Transition in the Intercalated Dichalcogenide	
Li_xZrSe_2	561
C. Berthier, Y. Chabre, P. Segransan, P. Deniard,	
L. Trichet and J. Rouxel	
1. Introduction	561
2. Samples	562
3. Semiconductor to metal transition	563
4. Ion ordering and ion-electron interaction	566
5. Conclusion	568
Acknowledgements	569
References	569
Charge Density Waves in the Mo Bronzes : CDW Transport in One Dimensional $\text{K}_{0.30}\text{MoO}_3$ and CDW Instability in Two-Dimensional $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$	571
J. Dumas, C. Escribe-Filippini, J. Marcus and C. Schlenker	
A Survey of the Origins of Incommensurate Behaviour and of New Materials Illuminating the CDW Field.....	575
J. A. Wilson	
Intercalation of Tetrathiafulvalene and Related Molecules into FeCl_3	585
S. M. Kauzlarich and B. A. Averill	
A Graphite Intercalation Compound as Applied to Battery Electrode Materials.....	586
A. J. Fischgrund	

IV - 2. Organic Conductors

Conducting Organic Solids.....	587
K. Bechgaard	
Organic Superconductors : Quasi-One-Dimensional Conductors, Anomalous Superconductors, Promising Materials.....	595
D. Jérôme	
1. Introduction	596
2. Electronic properties	598
3. An other plausible interpretation	614
References	621
Electronic Properties of Conjugated Polymers.....	625
R. H. Friend	
1. Introduction	625
2. Materials	627
3. Band and defect models	630
4. Polyacetylene - Experimental results	637
5. Other polymers	643
6. Conclusion	646
Acknowledgements	646
References	646
 <u>Important Discussion of Part IV-2</u>	
Unusual Electronic Soliton States of the Infinite Polyne Chain $\text{---} \text{C} = \text{C} \text{---} \text{x}$	653
M. J. Rice	
A Narrow Window for Superconductivity in Organic Conductors ..	655
S. S. P. Parkin	
Properties of Organic Salts of TMTSF and TMTTF.....	667
K. Mortensen	
1. Introduction	667
2. Role of the Hubbard U	668
3. Anion ordering	670
4. Conclusion	672
Acknowledgements	672
References	672

The Effects of Oxidation on the Electrical Properties of Organic Conjugated Polymers.....	675
J. R. Reynolds, J. C. W. Chien, D. J. Curran, F. E. Karasz, C. P. Lillya	
1. Introduction	675
2. Results and discussion	675
References	678
Anisotropy of Thermopower in $\text{MEM}(\text{TCNQ})_2$	679
M. Almeida, L. Alcácer and S. Oostra	

IV - 3 Inversion Layers

Localization and Interaction Effects in the 2D Electron Gas of the Silicon Inversion Layer.....	681
M. Pepper	

Important Discussion of Part IV - 3

The Effects of Hydrogen on MOS Structures.....	687
M. Evans, J. M. Noras, P. R. C. Stevens, C. B. Thomas	

Transport Theory for High-Resistivity Conductors.....	688
Dietrich Belitz and Walter Schirmacher	

XPS Investigation of the Electronic Structure of Highly Dispersed MnO on Carbon Foil.....	689
V. Young and L. Zhao	

Angle Resolved Photoemission and Secondary Electron Emission Study of Single Crystal Graphite.....	690
A. R. Law and H. P. Hughes	

IV - 4 Fast Ionic Conductors

Fast Ionic Conduction in Solids.....	691
J. B. Goodenough	

Phenomenology	691
Solid-solution electrodes	695
Solid electrolytes	702
References	712
What Factors May Increase Superionic Conductivity?.....715	
P. Hagenmuller	
List of Participants.....719	
Author Index.....725	
Subject Index.....727	