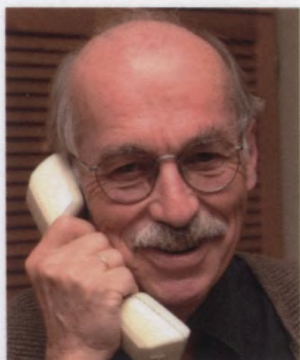


Research into the physical properties of organic solids, especially those containing conjugated π -electron systems, has developed into an active and attractive sub-area of solid-state physics over the last few decades.

There are several reasons for this development. First of all, there is the enormous diversity of properties typical of organic solids, such as long-distance energy transfer via excitons without electric-charge transport. With the powerful methods of organic chemistry, it is possible to vary these properties over wide ranges with "tailor-made" molecules. Secondly, new applications are under development, such as organic light-emitting diodes and novel molecular electronics, which supplement electronic components based on inorganic semiconductors. Finally, organic solids represent a link between traditional physics and biological physics: Organic solid-state physics has made important contributions to the clarification of the elementary processes of photosynthesis, for example.

This textbook has been written for graduate students and researchers, but will also be an interesting and valuable information source for all physicists, physical chemists and chemists wishing to learn more about the fascinating variety of organic solids. It is an introduction to the fundamentals of this topic, featuring detailed references and problems.



Professor Markus Schwöerer studied physics at the ETH Zurich, Switzerland, and at the University of Stuttgart, Germany, where he received his Ph.D. in 1967. In 1975, he accepted a professorship for experimental physics at the University of Bayreuth. He received the Annual Award for Chemistry from the Academy of Science at Göttingen in 1974. From 1996 to 1998, Professor Schwöerer was President of the German Physical Society (DPG). His main research interest is the physics of organic solids.



Professor Hans Christoph Wolf studied physics, chemistry and biology in Freiburg and Tübingen, both Germany, where he received his Ph.D. in 1952. From 1952 to 1954, he worked as a researcher in physical chemistry at the Technical University of Munich. After several years as an assistant professor, he was awarded a full professorship at the Third Physical Institute of the University of Stuttgart, of which he also became director, and from which he retired in 1997. Professor Wolf received the Otto Hahn Award of the German Physical Society and the Society of German Chemists (GDCh) in 2000. He was a member of the editorial boards of numerous international journals and is one of the most renowned and established authors in the fields of atomic and molecular physics. His field of research is the physics of organic solids.



1	Introduction	1
1.1	What are Organic Solids?	1
1.2	What are the Special Characteristics of Organic Solids?	9
1.3	Goals and Future Outlook	15
	Problems for Chapter 1	16
	Literature	24
2	Forces and Structures	25
2.1	Forces	25
2.1.1	Inductive Forces	26
2.1.2	Van der Waals Forces	27
2.1.3	Repulsive Forces	29
2.1.4	Intermolecular Potentials	30
2.1.5	Coulomb Forces	33
2.2	Structures	34
2.2.1	Crystals of Nonpolar Molecules	34
2.2.2	Crystals of Molecules with Polar Substituents	39
2.2.3	Crystals with a Low Packing Density, Clathrates	40
2.2.4	Crystals of Molecules with Charge Transfer, Radical-ion Salts	42
2.3	Polymer Single Crystals: Diacetylenes	43
2.4	Thin Films	47
2.5	Inorganic-Organic Hybrid Crystals	51
	Problems for Chapter 2	52
	Literature	54
3	Purification of Materials, Crystal Growth and Preparation of Thin Films	57
3.1	Purification	57
3.2	Highest Purity	61

3.3	Crystal Growth	63
3.4	Mixed Crystals	70
3.5	Epitaxy, Ultrathin Films	71
	Problems for Chapter 3	72
	References	73
4	Impurities and Defects	75
4.1	Foreign Molecules, Impurities, and X traps	75
4.2	Structural Defects	78
4.2.1	Point Defects	78
4.2.2	Dislocations	79
4.2.3	Grain Boundaries	82
4.2.4	Dipolar Disorder	83
4.3	Characterisation and Analysis of Impurities	84
4.4	Characterisation of Defects	84
	Literature	86
5	Molecular and Lattice Dynamics in Organic Molecular Crystals	89
5.1	Introduction	89
5.2	Intramolecular Vibrations	91
5.3	Phonons	93
5.3.1	The Eigenvector	94
5.3.2	The Wavevector	95
5.3.3	The Frequencies Ω (K)	96
5.3.4	Excitations	97
5.4	Experimental Methods	97
5.4.1	Inelastic Neutron Scattering	97
5.4.2	Raman Scattering and Infrared Absorption	99
5.5	The 12 External Phonons of the Naphthalene Crystal	100
5.5.1	Dispersion relations	100
5.5.2	Pressure and Temperature Dependencies	104
5.6	Analytic Formulation of the Lattice Dynamics in Molecular Crystals	107
5.7	Phonons in other Molecular Crystals	109
5.8	Hindered Rotation and Diffusion	113
5.8.1	Nuclear Magnetic Resonance	113
5.8.2	Benzene Crystals	116
5.8.3	Methyl Groups	118
5.8.4	Diffusion	120
	Problems for Chapter 5	122
	References	123

6	Electronic Excited States, Excitons, Energy Transfer	125
6.1	Introduction	125
6.2	Some historical remarks	126
6.3	Optical Excited States in Crystals	127
6.4	Davydov Splitting and Mini-Excitons	134
6.5	Frenkel Excitons	139
6.5.1	Excitonic States, Fundamental Equations	140
6.5.2	Polarisation and Band Structure	143
6.5.3	Coherence	147
6.6	Charge Transfer (CT) Excitons	149
6.7	Surface Excitons	153
6.8	Excimers	154
6.9	Exciton Processes, Energy Conduction	156
6.9.1	Sensitised Fluorescence	157
6.9.2	Delayed Fluorescence by Triplet Excitons	160
6.9.3	Excitonic Processes	163
6.10	Excitonic Processes in other Systems	171
6.11	Future Developments	173
	Problems for Chapter 6	173
	Literature	174
7	Structure and Dynamics of Triplet States	177
7.1	Introduction and Historical Remarks	177
7.2	Spin Quantisation in Triplet States	181
7.3	The Dipole-Dipole Interaction, Fine Structure	183
7.3.1	Zero Field ($B_0 = 0$)	183
7.3.2	Zeeman Splitting ($B_0 \neq 0$)	189
7.3.3	Powder Spectra	191
7.4	Mini-Excitons	192
7.5	Triplet Excitons	199
7.5.1	Anthracene and Naphthalene Crystals: Two-dimensional Triplet Excitons	199
7.5.2	Dibromonaphthalene Crystals: coherent, one-dimensional Triplet Excitons	203
7.6	Optical Spin Polarisation (OEP)	204
7.7	Optical Nuclear-Spin Polarisation (ONP)	212
7.8	Perspectives	214
	Problems for Chapter 7	214
	Literature	215
8	Organic Semiconductors	217
8.1	Preliminary Historical Remarks	220
8.2	Conductivity and Mobility of nearly-free Charge Carriers	223

8.3	Charge Carriers in Organic Semiconductors: Polarons, Shallow Traps and Deep Traps	228
8.4	Generation of Charge Carriers and Charge Transport: Experimental Methods	234
8.4.1	The TOF Method: Gaussian Transport	234
8.4.2	Photogeneration of Charge Carriers	238
8.4.3	Contacts, Injection, Ejection, and Dark Currents	244
8.4.4	Space-Charge Limited Currents	255
8.5	Charge-Carrier Mobilities in Organic Molecular Crystals	263
8.5.1	Band- or Hopping Conductivity?	263
8.5.2	Temperature Dependence and Anisotropy of the Mobilities	265
8.5.3	Electric-field Dependence	269
8.5.4	Band Structures	272
8.5.5	Charge-Carrier Traps	277
8.6	Charge Transport in Disordered Organic Semiconductors	279
8.6.1	The Bässler Model	282
8.6.2	Mobilities in High-Purity Films: Temperature, Electric-Field, and Time Dependence	284
8.6.3	Binary Systems	289
8.6.4	Discotic Liquid Crystals	290
8.6.5	Stationary Dark Currents	292
	Problems for Chapter 8	303
	Literature	303
9	Organic Crystals of High Conductivity	307
9.1	Donor-Acceptor Systems	307
9.2	Strong CT Complexes, Radical-ion Salts	308
9.3	The Organic Metal TTF-TCNQ – Peierls Transition and Charge-Density Waves	314
9.4	Other Radical-ion Salts and CT Complexes	322
9.5	Radical-Anion Salts of DCNQI	323
9.6	Radical-Cation Salts of the Arenes	330
9.6.1	Direct-current Conductivity	330
9.6.2	X-Ray Scattering	334
9.6.3	Optical Reflection Spectrum	335
9.6.4	Magnetic Susceptibility	337
9.6.5	Spin Resonance of the Conduction Electrons (ESR)	339
9.6.6	Charge-Density-Wave Transport	343
	Problems for Chapter 9	346
	Literature	347
10	Organic Superconductors	351
10.1	Introduction	351

10.2	Mainly One-dimensional Charge-Transfer Salts as Superconductors; Bechgaard Salts	353
10.3	Quasi-Two-dimensional Charge-Transfer Systems as Superconductors	356
10.4	The Nature of the Superconducting State in Organic Salts	359
10.5	Three-dimensional Superconductivity in Fullerene Compounds Literature	361 363

11	Electroluminescence and the Photovoltaic Effect	365
11.1	Electroluminescence: Organic Light-Emitting Diodes (OLEDs)	366
11.1.1	Historical Remarks	366
11.1.2	The Principle of the OLED	368
11.1.3	Multilayer OLEDs	373
11.1.4	Electro-optical Properties	377
11.2	Photovoltaic Effect: Organic Photovoltaic Cells	381
11.2.1	Exciton Dissociation	382
11.2.2	Photovoltaic Characteristics	384
11.2.3	CuPc/C ₆₀ Solar Cells Literature	386 389

12	Towards a Molecular Electronics	391
12.1	What is Molecular Electronics and What Will it Do?	391
12.2	Molecules as Switches, Photochromic Effects	392
12.3	Molecular Wires	395
12.4	Light-Induced Phase Transitions	396
12.5	Molecular Rectifiers	400
12.6	Molecular Transistors	401
12.7	Molecular Storage Units	406

Appendix: Coloured Plates	411
----------------------------------	------------

Index	417
--------------	------------