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Narrow-Gap Semiconductors

G. Nimtz and B. Schlicht
Narrow-Gap Lead Salts

R. Dornhaus and G. Nimtz
The Properties and Applications of the
 $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Alloy System



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Narrow-Gap Semiconductors

Contributions by

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With 244 Figures



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* denotes a volume which contains a Classified Index starting from Volume 36.

Preface

This volume is devoted to various narrow gap semiconductors which are very important for both basic solid state physics and infrared devices. The first contribution reviews the properties of IV-VI compound lead salts, the second one those of mercury cadmium telluride. The latter contribution was originally published first 1976 in Volume 78 of the Springer Tracts in Modern Physics. Since that time the research on this II-VI alloy has not ceased, however, the main interest has now switched to topics as for instance the epitaxial growth of crystals, the transport properties and the recombination behaviour of p-type crystals, and last but not least to the analysis of surface and interfaces. As that volume 78 is sold out, this contribution is reprinted with supplements to various sections that contain some of the data published quite recently. We added also some new sections, which consider the changed spectrum of research on this alloy. (These supplements are indicated by vertical stripes on the page margin.) We would like to mention three other review articles published quite recently on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ dealing with "Magneto-optical Properties" by M.H. Weiler, "Nonlinear Optical Effects" by T.W. Kruse and J.F. Ready, and "Growth, Properties and Applications" by H. Maier and J. Hesse.*

We would like to apologize for using in the lead salt article a citation system different from that in the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ one. The reason for doing so against the publisher's esthetic arguments is, that the system used in the lead salt article seems to us more comfortable for both the reader and the author.

Finally we would like to acknowledge gratefully the patience and the support in preparing this volume by the Editors Prof. Dr. G. Höhler and Prof. Dr. E.A. Niekisch. To Miss Therese Becker, Mrs. Gisela Hahn, Mrs. Hilde Latta, Mrs. Inge Kirschke, Miss Ruth Küpper, and Mrs. Inge Simons we wish to express our appreciation and thanks for their assistance in the preparation of this volume.

Cologne, April 1983

*R. Dornhaus
G. Nimtz
B. Schlicht*

* WEILER /367/, KRUSE and READY /368/, MAIER and HESSE /369/

K. Seeger

Semiconductor Physics

An Introduction

2nd corrected and updated edition. 1982.
288 figures. XII, 462 pages
(Springer Series in Solid-State Sciences, Volume 40)
ISBN 3-540-11421-1

Contents: Elementary Properties of Semiconductors. – Energy Band Structure. – Semiconductor Statistics. – Charge and Energy Transport in a Non-degenerate Electron Gas. – Carrier Diffusion Processes. – Scattering Processes in a Spherical One-Valley Model. – Charge Transport and Scattering Processes in the Many-Valley Model. – Carrier Transport in the Warped-Sphere Model. – Quantum Effects in Transport Phenomena. – Impact Ionization and Avalanche Breakdown. – Optical Absorption and Reflection. – Photoconductivity. – Light Generation by Semiconductors. – Properties of the Surface. – Miscellaneous Semiconductors. – Appendix: Physical Constants. – References. – Subject Index.

O. Madelung

Introduction to Solid-State Theory

Translated from the German by B. C. Taylor
1978. 144 figures. XI, 486 pages
(Springer Series in Solid-State Sciences, Volume 2)
ISBN 3-540-08516-5

Contents: Fundamentals. – The One-Electron Approximation. – Elementary Excitations. – Electron-Phonon Interaction: Transport Phenomena. – Electron-Electron Interaction by Exchange of Virtual Phonons: Superconductivity. – Interaction with Photons: Optics. – Phonon-Phonon Interaction: Thermal Properties. – Local Description of Solid-State Properties. – Localized States. – Disorder. – Appendix: The Occupation Number Representation. – References. – Subject Index.

R. H. Kingston

Detection of Optical and Infrared Radiation

1978. 39 figures, 2 tables. VIII, 140 pages
(Springer Series in Optical Sciences, Volume 10)
ISBN 3-540-08617-X

Contents: Thermal Radiation and Electromagnetic Modes. – The Ideal Photon Detector. – Coherent or Heterodyne Detection. – Amplifier Noise and Its Effect on Detector Performance. – Vacuum Photodetectors. – Noise and Efficiency of Semiconductor Devices. – Thermal Detection. – Laser Preamplification. – The Effects of Atmospheric Turbulence. – Detection Statistics. – Selected Applications.

Optical and Infrared Detectors

Editor: **R. J. Keyes**

2nd corrected and updated edition. 1980. 115 figures, 14 tables. XI, 325 pages
(Topics in Applied Physics, Volume 19)
ISBN 3-540-10176-4

Contents: *R. J. Keyes:* Introduction. – *P. W. Kruse:* The Photon Detection Process. – *E. H. Putley:* Thermal Detectors. – *D. Long:* Photovoltaic and Photoconductive Infrared Detectors. – *H. R. Zwicker:* Photoemissive Detectors. – *A. F. Milton:* Charge Transfer Devices for Infrared Imaging. – *M. C. Teich:* Non-linear Heterodyne Detection. – *R. J. Keyes:* Recent Advances in Optical and Infrared Detector Technology.



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Semiconductor Devices

for Optical Communication

Editor: **H. Kressel**

2nd updated edition. 1982. 191 figures.

XIV, 309 pages

(Topics in Applied Physics, Volume 39)

ISBN 3-540-11348-7

Contents: *H. Kressel:* Introduction. – *H. Kressel, M. Ettenberg, J. P. Wittke, I. Ladany:* Laser Diodes and LEDs for Fiber Optical Communication. – *D. P. Schinke, R. G. Smith, A. R. Hartmann:* Photodetectors. – *R. G. Smith, S. D. Personick:* Receiver Design for Optical Fiber Communication Systems. – *P. W. Shumate, Jr., M. DiDomenico, Jr.:* Lightwave Transmitters. – *M. K. Barnoski:* Fiber Couplers. – *G. Arnold, P. Russer, K. Petermann:* Modulation of Laser Diodes. – *J. K. Butler:* The Effect of Junction Heating on Laser Linearity and Harmonic Distortion. – *J. H. Mullins:* An Illustrative Optical Communication System. – *H. Kressel, M. Ettenberg:* Light Sources – an Update. – *R. G. Smith:* Photodetectors and Receivers – an Update. – Subject Index.

R. G. Hunsperger

Integrated Optics: Theory and Technology

1982. 167 figures. XIV, 299 pages

(Springer Series in Optical Sciences, Volume 33)

ISBN 3-540-11667-2

Contents: Introduction. – Optical Waveguide Modes. – Theory of Optical Waveguides. – Waveguide Fabrication Techniques. – Losses in Optical Waveguides. – Waveguide Input and Output Couplers. – Coupling Between Waveguides. – Electro-Optic Modulators. – Acousto-Optic Modulators. – Basic Principles of Light Emission in Semiconductors. – Semiconductor Lasers. – Heterostructure, Confined-Field Lasers. – Distributed Feedback Lasers. – Direct Modulation of Semiconductor Lasers. – Integrated Optical Detectors. – Applications of Integrated Optics and Current Trends. – References. – Subject Index.

Insulating Films on Semiconductors

Proceedings of the Second International Conference, INFOS 81, Erlangen, Federal Republic of Germany, April 27–29, 1981

Editors: **M. Schulz, G. Pensl**

1981. 240 figures. X, 316 pages

(Springer Series in Electrophysics, Volume 7)

ISBN 3-540-11021-6

Contents: Si-SiO₂ Interface. – Thin Insulating Films. – Charge Injection Into Insulators. – Multilayer Structures. – Interface Characterization Techniques. – Breakdown and Instability of the SiO₂-Si System. – Technology. – Laser Processing. – Transport Properties in Inversion Layers. – Films on Compound Semiconductors. – Index of Contributors.

Ion Implantation Techniques

Lectures given at the Ion Implantation School in Connection with the Fourth International Conference on Ion Implantation: Equipment and Techniques

Berchtesgaden, Federal Republic of Germany, September 13–15, 1982

Editors: **H. Ryssel, H. Glawischnig**

1982. 245 figures. XII, 372 pages

(Springer Series in Electrophysics, Volume 10)

ISBN 3-540-11878-0

Contents: Machine Aspects of Ion Implantation: Ion Implantation System Concepts. Ion Sources. Faraday Cup Designs for Ion Implantation. Safety and Ion Implanters. – Ion Ranges in Solids: The Stopping and Range of Ions in Solids. The Calculation of Ion Ranges in Solids with Analytic Solutions. Range Distributions. – Measuring Techniques and Annealing: Electrical Measuring Techniques. Wafer Mapping Techniques for Characterization of Ion Implantation Processing. Non-Electrical Measuring Techniques. Annealing and Residual Damage. – Appendix: Modern Ion Implantation Equipment: Evolution and Performance of the Nova NV-10 PredepTM Implanter. Ion Implantation Equipment from Veeco. The Series IIIA and IIIX Ion Implanters. Standard High-Voltage Power Supplies for Ion Implantation. The IONMICROPROBE A-DIDA 3000-30 for Dopant Depth Profiling and Impurity Bulk Analysis. – List of Contributors. – Subject Index.



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Narrow-Gap Lead Salts

By G. Nimtz and B. Schlicht

1. Introduction

The narrow-gap semiconductors among the family of IV-VI compounds and their pseudo-binary alloys show some extraordinary aspects of solid-state physics. The polymorphism of IV-VI compounds indicate the inherent structural instability which is based on the average five valence electrons. The most interesting point, however, is that the bonds are based on the itinerant electrons in the valence band which is separated from the conduction band by a narrow energy gap. In such a situation one expects the electronic properties to be strongly correlated with the lattice instability. Another interesting feature follows from the many-valley band structure in combination with a strongly non-isotropic effective mass in lead telluride: the Auger mechanism is expected to play a dominant role in free-carrier recombination.

During the last twenty years many experimental and theoretical studies were performed to elucidate the basic properties of the IV-VI compounds. In addition many activities in the field of infrared devices have been successful in producing laser diodes and photodetectors for the wavelength range between 4 and 30 μm .

It is our intention to present in this article the basic data of the lead salt narrow gap semiconductors currently available. We should like to encourage further efforts towards a better understanding of this fascinating semiconductor family, and supply data for the development of efficient devices. We are aware of the fact that this article is not a complete presentation of all investigations published so far.

2. The Crystal

This chapter is devoted to the basic physical properties of the four lead salt narrow-gap alloys $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$, $\text{PbS}_{1-x}\text{Se}_x$, and $\text{PbTe}_{1-x}\text{S}_x$ and their binary compounds. In the first section the lattice, elastic and related data are presented. The lattice instability representing one of the outstanding physical properties of these IV-VI binary and ternary compounds is also discussed in this section. In the second section phase diagrams are introduced, and the third section deals with lattice imperfections and their properties.

2.1 Basic Properties

The narrow-gap lead salt alloys are more or less ionic crystals. The ionicity decreases in going from PbS to PbSe to PbTe. The ionic nature of the bonding of the lead chalcogenides is impressively shown by the spatial valence charge distributions.

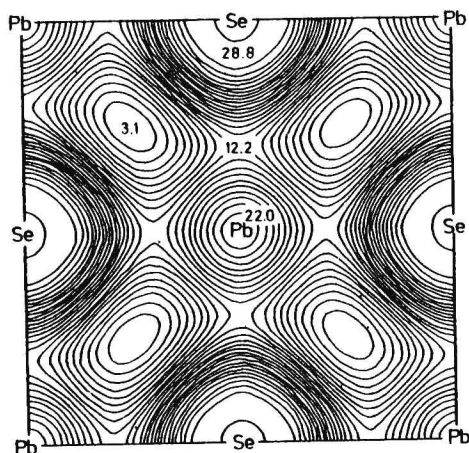


Fig. 2.1. The total valence electron charge density for PbSe derived from pseudopotential band-structure calculations. The values are given in units of electrons per unit-cell volume. The charge around the cation sites is mainly of s character whereas around the anion sites it clearly exhibits contributions from both s and p states /75S1/

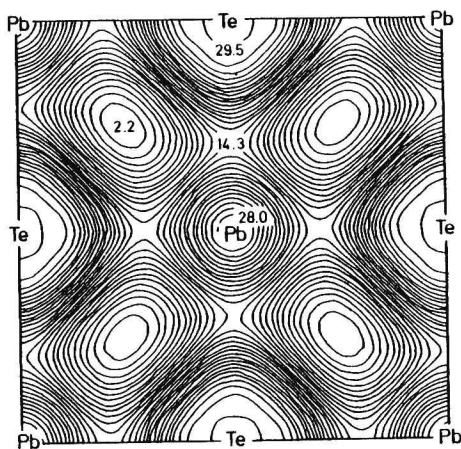


Fig. 2.2. The total valence electron charge density for PbTe derived from pseudopotential band-structure calculations. The values are given in units of electrons per unit-cell volume. The charge around the cation sites is mainly of s character whereas around the anion sites it clearly exhibits contributions from both s and p states /75S1/

SCHLÜTER et al. /75S1/ have calculated the contours of constant charge density in a (100) plane for various bands. The results for the sum of the five valence bands are shown in Fig. 2.1 for PbSe and in Fig. 2.2 for PbTe. In Table 2.1 the calculated approximate fractional charges inside touching spheres around anions and cations decomposed into $l = 0, 1, 2$ angular components, are given for the valence bands /75S1/. From these an approximate charge transfer of 1.9 (PbSe) and 1.5 (PbTe) electrons from cation to anion can be estimated (in the "totally ionic" model two electrons of the cation are transferred to the anion).

Most of the binary compounds, e.g. PbTe, PbS, PbSe, SnTe are found to be isomorphous with rocksalt, its lattice is shown in Fig. 2.3. The low molecular weight material SnSe, on the other hand, is found in an orthorhombic structure (Fig. 2.4). The nature of chemical binding in these crystals is mixed ionic-covalent. The phy-

Table 2.1. Calculated fractional charges (in percent) inside touching spheres around anions and cations. The sphere radii were chosen as $r_{\text{cation}} = 1.29 \text{ \AA}$, $r_{\text{anion}} = 1.94 \text{ \AA}$ for PbTe and $r_{\text{cation}} = 1.22 \text{ \AA}$, $r_{\text{anion}} = 1.83 \text{ \AA}$ for PbSe (from /75S1/)

Band	PbSe						PbTe					
	Pb			Se			Pb			Te		
	s	p	d	s	p	d	s	p	d	s	p	d
1	1	1	0	97	1	0	3	1	0	95	1	0
2	55	0	0	18	24	3	70	0	0	13	13	4
3 - 5	9	7	1	1	78	4	5	9	2	0	80	4
1 - 5	16	4	1	23	52	4	18	6	1	22	50	3
	21			79			25			75		
Simple ionic	20	0	0	20	60	0	20	0	0	20	60	0

sical background of the crystal structure of IV-VI compounds was recently discussed extensively in papers by LITTLEWOOD /80L1/. The covalent binding is assumed to be predominant which is concluded for instance from analysis of carrier scattering /70R/. Investigations of the carrier scattering in various lead chalcogenides have shown that both optical and acoustical phonons are important, the latter being an indication of predominant covalent binding.

All the compounds with NaCl structure have a structural phase transition due to their mixed ionic-covalent chemical binding. With decreasing ionicity the NaCl structure becomes more and more unstable, accompanied by both an increasing electronic

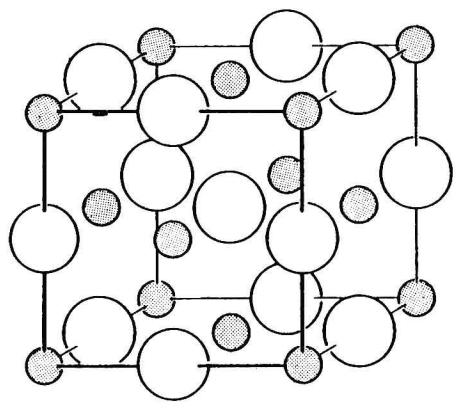


Fig. 2.3. The rocksalt structure

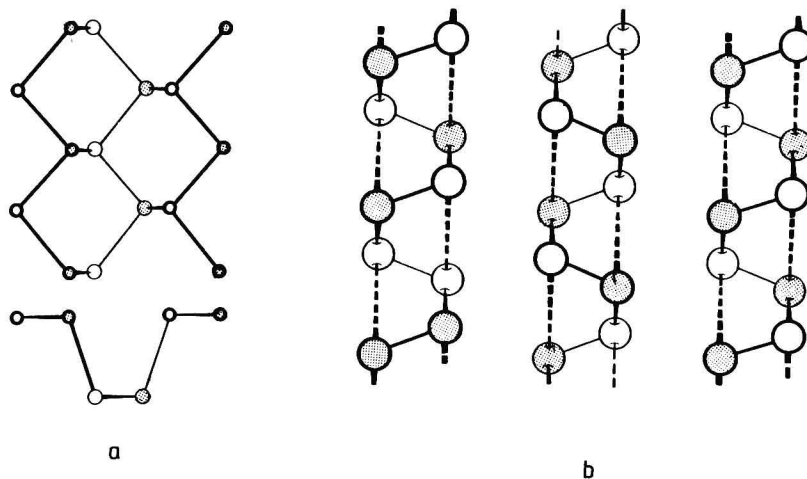


Fig. 2.4a,b. Sketch of an orthorhombic lattice (a) ground plan and front elevation, thick and thin circles indicate the atom is above or below the plane of the paper, respectively, (b) projection on the (100) plane

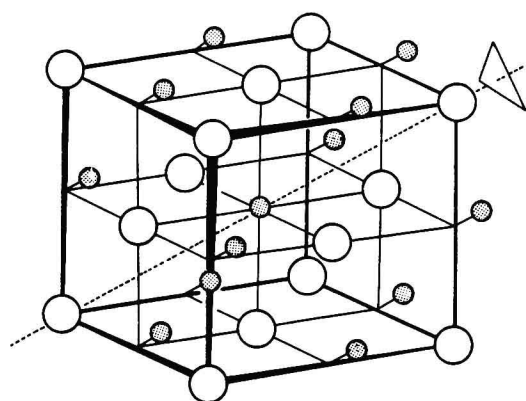


Fig. 2.5. The As-type rhombohedral structure

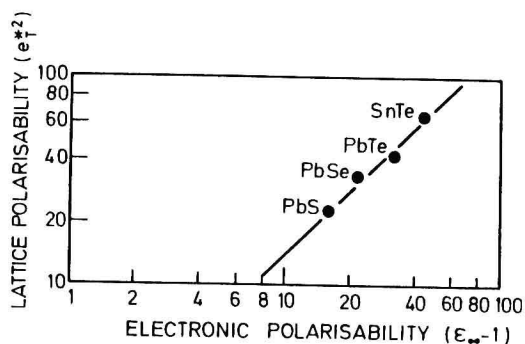


Fig. 2.6. Lattice polarisability ($e^*{}^2$) vs electronic polarisability ($\epsilon_{\infty} - 1$) for some IV-VI compounds with rocksalt structure /73L2/

and lattice polarisability /77L5/. This behaviour is shown in Fig. 2.6 and will be discussed in more detail in Sect. 5.4.

The cubic to rhombohedral phase transition can be explained as a result of a large electron-TO phonon coupling due to the resonant nature of the half-filled p states. Below the transition temperature T_C (for most of the compounds $T_C < 0$ holds as will be shown below) the two neighbouring ions along the $\langle 111 \rangle$ axis make displacements in opposite directions forming a rhombohedral, As-type crystal structure as shown in Fig. 2.5. The cubic rocksalt structure of the lead chalcogenides is stabilised by perpendicular p bonds, with the s states fully occupied and making only a small contribution to the bonding. The lack of hybridisation between the s and p bands in the lead salts arises from the large energy splitting between s and p states. The rhombohedral structure is an intrinsic instability of the unsaturated p bonds in the rocksalt structure. Because there are only six p electrons per atom pair, and yet there are six neighbours for each atom, the p bonds are unsaturated. The rocksalt structure is thus a resonantly bonded system /68K1, 73L2/ in which the bonding electrons are relatively free to move from the bond on one side of the atom to the bond on the opposite side in response to an external field. In the rhombohedral phase the six cubic nearest neighbours are displaced along the $\langle 111 \rangle$ direction with respect to the central atom so that each atom now has three nearest neighbours and three second-nearest neighbours in the distorted phase. The nearest neighbours bond strongly together in a layer perpendicular to the $\langle 111 \rangle$ direction. The bonds in the rhombohedral structure are now more nearly saturated than in the cubic system, because the bonding electrons are localised in the nearest-neighbour bonds.

The cubic-rhombohedral phase transition can be understood as the result of the electron-TO phonon coupling for modes propagating in the $\langle 111 \rangle$ direction. Coupled to this is a shear which distorts the cube into a rhombohedron, and lengthens the $\langle 111 \rangle$ axis.

The orthorhombic structure found in SnSe arises because of the strong sp hybridisation in IV-VI compounds with low molecular weights /80L1/. The orthorhombic structure also seems to present the high pressure phase of IV-VI compounds and their alloys, which were found in the rocksalt structure at atmospheric pressure /e.g.: 40B, 48B, 54B, 67M, 68K3, 68W, 80S, 81S1/. Data of the lattice constants of the pressure induced orthorhombic structure of several IV-VI compounds are given in Table 2.2. From a study of this high pressure phase transition in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ SUSKI et al. /81S1/ conclude that a metallic-covalent transition takes place. They assume a promotion of an s electron to p states due to the decrease in interatomic distance.

Consequences for the transport properties as well as the accompanied softening of the transverse optical phonon due to the structural phase transition are discussed in Sects. 4.2 and 5.4 respectively. Experimental data of the transition temperature are shown for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ in Fig. 2.7. These data published by MURASE