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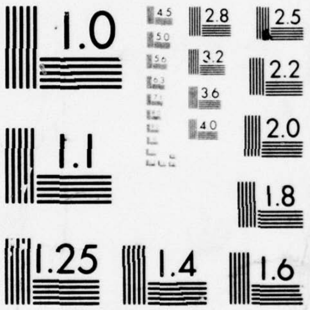
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ELECTRONIC PROPERTIES OF SOLIDS

ELECTRONICS RESEARCH BRANCH
ELECTRONIC TECHNOLOGY DIVISION

JANUARY 1977

TECHNICAL REPORT AFAL-TR-76-155
FINAL REPORT FOR PERIOD 1 JULY 1964 - 30 JUNE 1974

Approved for public release; distribution unlimited

AIR FORCE AVIONICS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

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Solid State devices have been widely used in the electronics area for many years and more recently are being used extensively in the electro-optic field. The properties of these devices depend strongly on the material properties, of the semiconductor from which they are produced. The investigations in this work unit were concentrated on several wide band gap materials composed of elements from group II and group VI of the periodic table. The approach centered around studying the basic properties of the pure material and also the effect of doping impurities. The investigations from this work unit have had an impact

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in the scientific community by providing a large number of material constants which clarify the electronic and electro-optic behavior of these materials. They have also uncovered new phenomena, new research approaches and material parameters useful in testing specialized aspects of the theory of solids.

PREFACE

This final report of project 7885 0302 covers the period of 1 July 1964 to 30 June 1974. It describes the research conducted on the Electronic Properties of Solids. The two major areas of concern were the investigation of the properties of ideal crystals and the properties of impurities and defects in II-VI semiconductors. It was the purpose of the work to relate the electronic and optical properties of semiconductor materials with those parameters which describe the atomic and structural properties of the constituent elements.

This report does not deal with the details of the experimentation but instead describes the purpose and results of such investigations. The details can be found in the publications listed in the appendix.

The impact that these investigations have had on the scientific community can not be expressed in the few pages of this report. The large list of publications in the appendix, however, is real proof not only of the superior quality of work that was performed but also of the need for such information in the scientific community.

TABLE OF CONTENTS

SECTION I

INTRODUCTION

Solid State devices are desirable components in the electronics and electro-optic equipment field. They fulfill a variety of functions as transistors, diodes, photodetectors, light emitting diodes, and logic devices to name just a few. Yet, whether as individual components or in larger assemblies like integrated circuits, there are only few basic materials (Germanium, Silicon, and lately some III-V Compounds) which were used in the commercial manufacturing process. This development has been the consequence of an empirical approach of the study of semiconductivity materials. Simultaneously and subsequently basic research efforts were initiated in order to relate the electronic and optic responses of the materials with those parameter which in turn can be related to the atomic species and the structure of which these materials are composed. The rationale for this approach is that with an establishment of such relations predictions of the electronic and optic properties of other materials can be made prior to their synthesis.

In this work unit the basis of such investigations was expanded to include the wideband gap semiconductors composed of elements of the II and VI group of the periodic table, particularly CdS, ZnS, CdSe, ZnSe, and ZnO. The approach was twofold; it included a) the study of the basic properties of the pure materials and b) the effect induced by certain impurities. In both cases the observable properties, like optical constants, conductivity, light emission spectra, and electron emission spectra, were related to theoretically devised models and supplied a variety of material constants. They served as empirical parameter for further theoretical predictions or if compared with ab initio theoretical calculations, as standard for the evaluation of the quality of results obtained by the different theories, i.e., as experimental control for the validity or quality of the different assumptions and approximations which entered theoretical calculations.

This final report will not deal with the details of the executions of the different investigations nor with the related calculations. For these details the reader is referred to the separate publications which resulted from this work and which are listed with their abstracts in the appendix.

The work performed in this research group has been highly influential in the scientific community: 1) It has provided a large number of material constants for II-VI and III-V semiconducting compounds which clarified the electronic and opto-electronic behavior of these materials and pointed out their device potentials. 2) It drew attention to new physical phenomena like the "induced absorption". 3) New experimental approaches have been used by other investigators for the research on other materials. 4) Its results have been useful in testing a variety of theoretical treatments and specialized aspects of the theory of solid state materials.

Section II deals with the combinations to the analysis of pure materials. In Section III the investigated properties of impurities and their effects due to their chemical value and their interaction with the host lattice are reported on.

SECTION II

PROPERTIES OF IDEAL CRYSTALS (BANDSTRUCTURE PARAMETER)

The applicability of semiconductors for a variety of devices is based on the motions of electrons, or their transitions between discrete energy levels in an appropriate crystal. These discrete energy levels are analogous to the allowed energy levels of electrons in an isolated atom, i.e. to their different possible orbitals. Each kind of crystal exhibits an energy level scheme usually called "band structure" that is characteristic for its chemical composition and its crystallographic structure. Impurities, when added to the crystal, usually cause the presence of additional energy levels. The bandstructure and the impurity levels determine all and every electronic and optical property of a crystal.

Our knowledge today of such energy bands is derived from an enormous amount of data determined by experiments. Theoreticians, at present, have all the tools (e.g. quantum mechanics, theory of relativity) to predict electronic bandstructures in principle. In reality, however, even the biggest computers are not large and fast enough to do these calculations completely and exactly. Thus their main effort is centered around finding suitable approximations which make the calculations manageable and which still furnish reasonably exact results. Therefore calculations are made by various methods, mainly for crystals with relatively well determined experimental bandstructure parameters. The degree of agreement with experiments determines the validity of the method used for the calculation. In the case of semiconductors, such parameters used for comparison with theory or for adjustment of theory are usually energy differences between extrema of certain energy levels (i.e., bandgaps between conduction and valence bands at points of high symmetry in the momentum space). To obtain good agreement with experiment, theoreticians often feel free to adjust one or a few parameters. However plausible and correct those adjustments may be (they are usually justified as lump sum refinements of previously made approximations), one can not maintain that the resulting agreement with experimental bandstructure may not be purely accidental; i.e., that it is a convincing argument for the validity of theory and the approximations used.

PRESSURE EFFECTS ON BANDGAP SEPARATIONS

One simple and real acid test of bandstructure calculations, however, is possible by considering the effects of pressure on the system. Pressure causes a lattice dilation and a theoretician can proceed to recalculate, e.g. bandgaps, without further adjustments according to his original scheme by changing the lattice parameters by a small amount. Now the degree of agreement between measured and calculated pressure coefficients is a valid test for the value of the theory.

Besides aiding such "energing theories," pressure coefficients are useful in other ways too. To summarize what we gain by their knowledge:

1) In conjunction with a well established theory we can identify so called "symmetry assignments" of energy levels by observing the way in which they shift and (perhaps) split.

2) Knowledge of the dilation effect on certain levels (in conjunction with thermal expansion and compressibility coefficients) enables us to reduce experimentally determined temperature effects to their true, intrinsic value, because the effect of the thermal expansion is otherwise inseparable.

3) The pressure coefficient directly determines the amount of pressure necessary to obtain a given optical frequency variation e.g. in solid state lasers (say: pressure-tunable lasers) or in electro-optical crystals.

4) The pressure coefficient offers an invaluable check on emerging theories, as noted above. The primary purpose of this report is to show how our work contributes in this respect. In three examples I will show how our experimental results have interacted with theory and contributed to the present state of the art.

a) In the area of bandstructure calculations we have measured the pressure coefficients of bandgaps of several II-VI compounds (ZnO, ZnS, ZnSe, ZnTe, CdS, CdTe). Theory, though able to compute bandgaps fairly well, has not yet come up with the correct pressure coefficients and is thus forced to refine its original approach.

b) The binding theory of excitons is another area we're engaged in (An exciton is a hole in the valence band and an electron in the conduction band forming a hydrogen-like entity). Here we found experimentally a qualitative disagreement with theory. Energy levels split with pressure. This was not expected according to the conventional treatment. The results could be accounted for only after considering a spin exchange term which, in turn, is relevant also for the zero-pressure binding energy of excitons. The consequences of the presence of "exchange," demonstrated by these experiments, will be highly significant in all large bandgap semiconductors.

Conceptually the experiments are simple: One observes spectra in luminescence, absorption, or reflection. These spectra can be related to induced transitions of electrons between two energy levels of the crystal. One applies pressure, hydrostatic or uniaxial pressure, and records the shift in energy of said structure as a function of the applied pressure. The difficulties, however, become obvious when one tries to do just this. With those pressures, which one can easily achieve, there is no noticeable energy shift to be observed; and with very high pressures the optical accessibility of the sample becomes a problem. The minimum shift which is still observable also depends on the "linewidth" of the absorption lines or the reflection characteristics. Furthermore we set ourselves the goal of obtaining coefficients with less than 10% error (in order to be of value for the comparison with theory).

Our approaches were along two different lines, each with its own particular advantages and drawbacks: 1) application of hydrostatic pressure and 2) application of uniaxial pressure. In both cases it is advantageous to work and therefore the necessary pressure is lower. Also theories are generally worked out without the inclusion of lattice vibrations and, thus, we would be as close as possible a common basis with theory.

The hydrostatic system designed and built at ARL which finally did the job consisted of a pressure generator capable of compressing gas up to 20,000 atmospheres (about 300,000 PSI), and a test vessel with two windows which when submersed in a specially designed dewar could be used at the temperature of liquid nitrogen (-320 F). 1) Measurements with this test chamber have been routinely done at this temperature to about 12,000 atmospheres (about 180,000 PSI). Note that optical accessibility in this pressure and temperature range by itself was a unique technological achievement. Materials had to be used beyond their conventional design limits,and even apart from special problems of window seals the design area was technologically adventurous. For example, the window plug in the test vessel had to withstand a force equivalent to the weight of a B-52 bomber.

As a byproduct, or figure of merit for the system, we could establish the freezing point of helium at liquid nitrogen temperature (14,140 bars = 212,000 PSI). 2) The point was about 50% higher in pressure (and temperature) than the highest one measured otherwise. The apparatus still marks the design limit. It was copied by workers in the high pressure field and is working presently in Laboratories at Harvard University, University of Cambridge, England, and at the Sorbonne in Paris. The hydrostatic pressure coefficients measured were all measured to better than ± 5% error, some to ± 2%.

Uniaxial pressure applications do not have the glamour but also do not involve the difficulties of the hydrostatic techniques. No huge forces are required if the crystal area is reduced. Several different arrangements have been used: 1) placing a crystal at the extension of a hydraulic ramp, 2) bending a thin crystal, thus observing the effects of compression and expansion on the reflection spectra and, 3) pulling a crystal up to only 1/2-pound maximum. In this last case, for absorption spectra the crystal was not thicker than 2 micron 0.00004 inch). With a width of about 2 mm (0.08 inch) this again corresponds to a stress of about 5,000 atmospheres (or 75,000 PSI).

The limit here is set by the brittleness of the crystals, which usually break even before this stress is reached. Though we were able to work at still lower temperatures with uniaxial pressures by immersing the stress apparatus with the crystal into liquid helium (4 K or -452 F), the pressure coefficients could not be determined accurately because of the greater difficulties in determining the stress to better than 10%. Nevertheless this arrangement proved useful; because with uniaxial stress, cubic crystals and especially hexagonal crystals (as the wurtzite II-VI compounds which we were most interested in) give several nonequivalent directions to apply the stress to and, thus, several pressure coefficients to compare with theory.

In the study of semiconductors we studied band-to-band transitions usually by measuring the characteristic structure in the reflection spectra. Figure 1 gives an example of such structure and the change (the energy-shift) as a function of hydrostatic pressure. The electronic transition in this example does not correspond to the fundamental bandgap of CdTe, but to a higher one, the so called E_1 gap. Figure 2 demonstrates the bandstructure of CdTe as calculated by k.p method. The three heavy arrows E_0, E_1 and $E_1+\Delta_1$ indicate the gaps on which we investigated the pressure coefficients. This figure also may serve to indicate how much information the calculated bandstructure may offer. The few parameters available as experimental checks are a few vertical band separations and curvatures at the top of the valence band and at the bottom of the conduction band at the Γ point.

Figure 3 shows an example of the evaluation of two sets of measurements in CdTe resulting in pressure coefficients for the transition and the $L_{3v} \rightarrow L_{1c}$ transitions, also called E_1 and $E_1 + \Delta_1$ where the small splitting Δ_1 is the spin-orbit splitting of the valence band at the L point. This assignment had been supported also be the pressure coefficients, for $E_1 + \Delta_1$ have very similar pressure coefficients. This denotes that the transitions do not occur at different symmetry points in the momentum space but at one and the same point between a split band and a single band, because the spin-orbit splitting of the valence band is not expected to change appreciably with pressure.

Similarly, as demonstrated in the above example, we measured the hydrostatic pressure coefficients for a variety of II-VI compounds. These coefficients are summarized in Table 1.

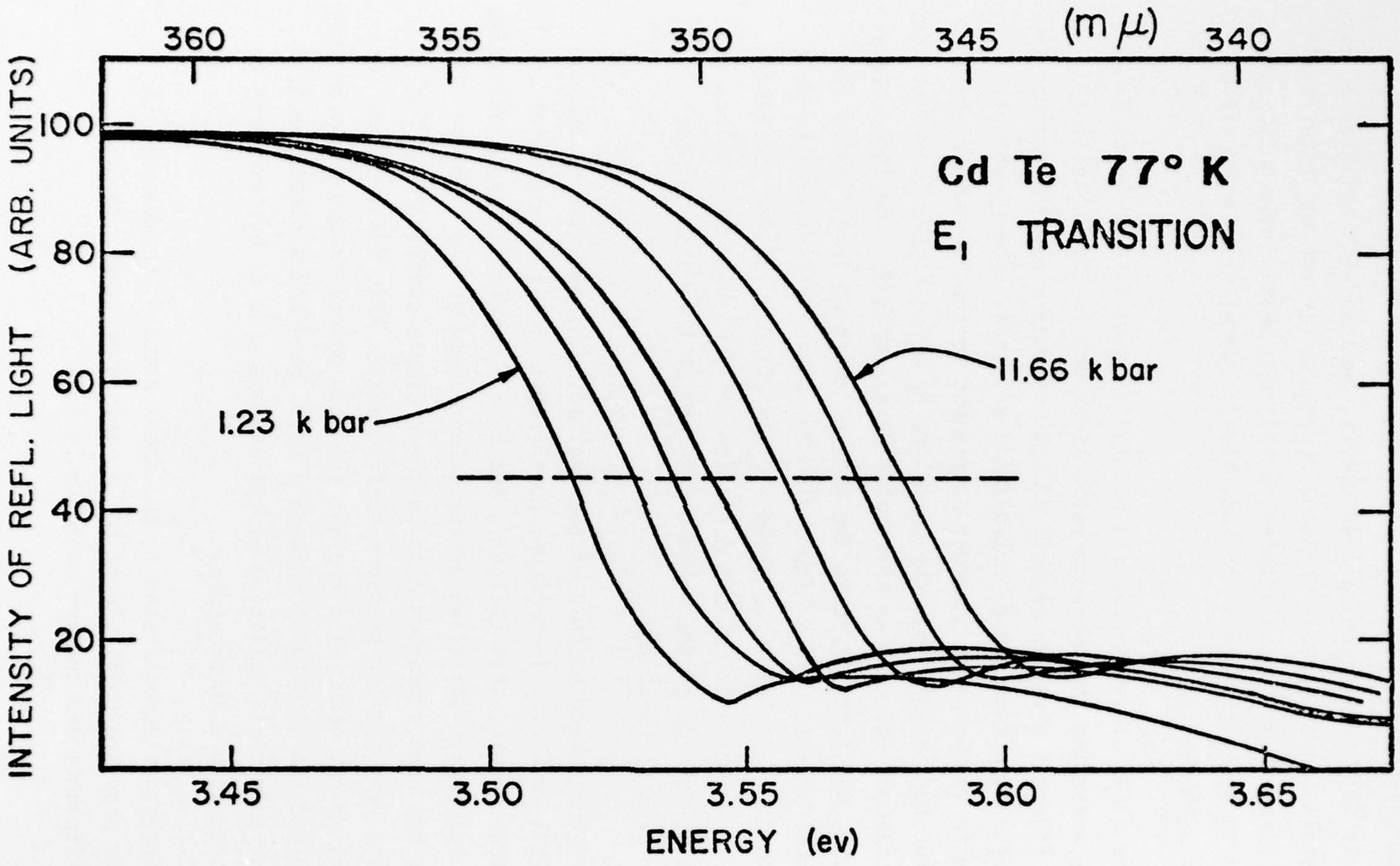

Figure 1. A Typical "Reflectivity Characteristic" and its Dependence on Hydrostatic Pressure. It corresponds to the E_1 transition in cadmium telluride.

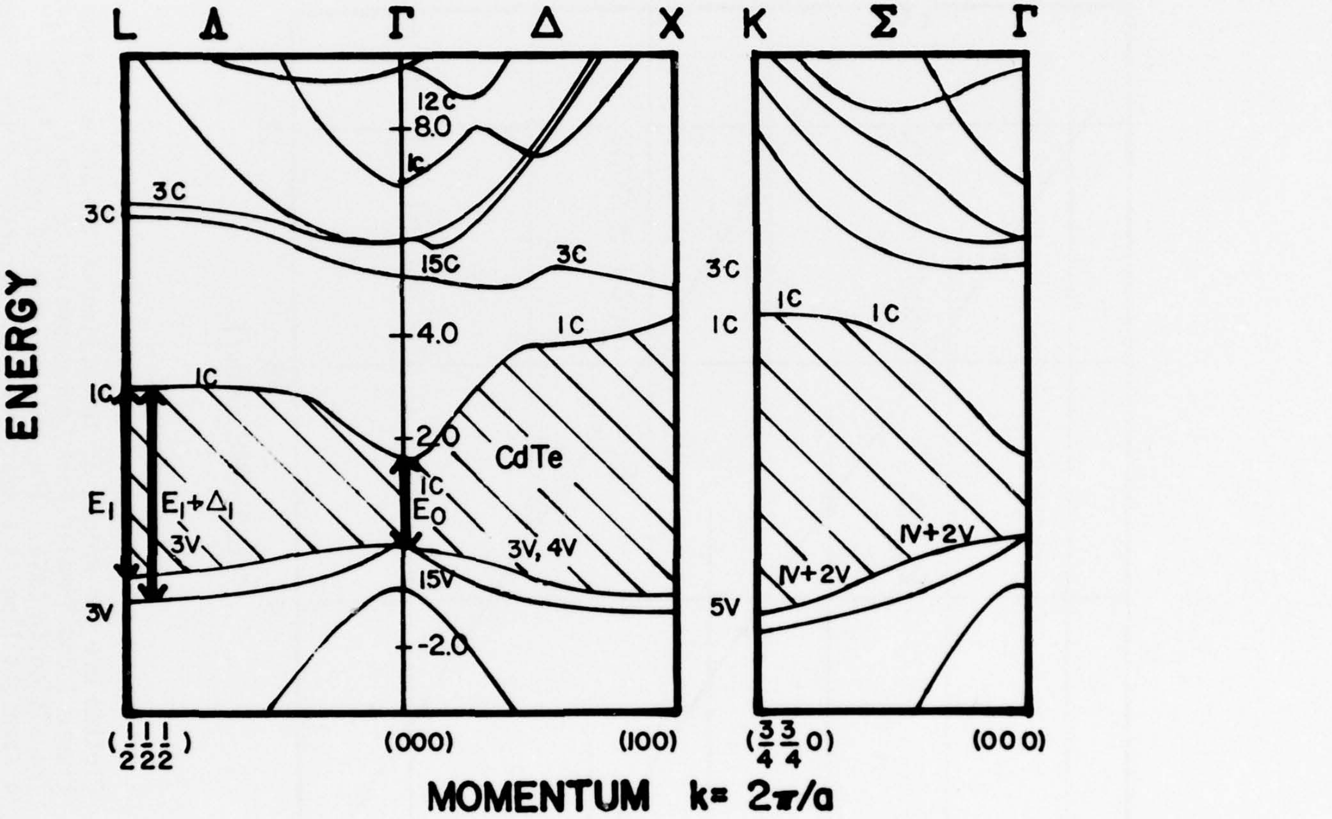

Figure 2. The Band Structure of Cadmium Telluride as Computed by M. Cardona According to the k.p Method. The shaded area is the forbidden gap. Letters designate preferred symmetry points in the momentum space (Brillouin zone). The pressure coefficients of the transitions E_0, E_1 and $E_1 + \Delta_1$ were determined.

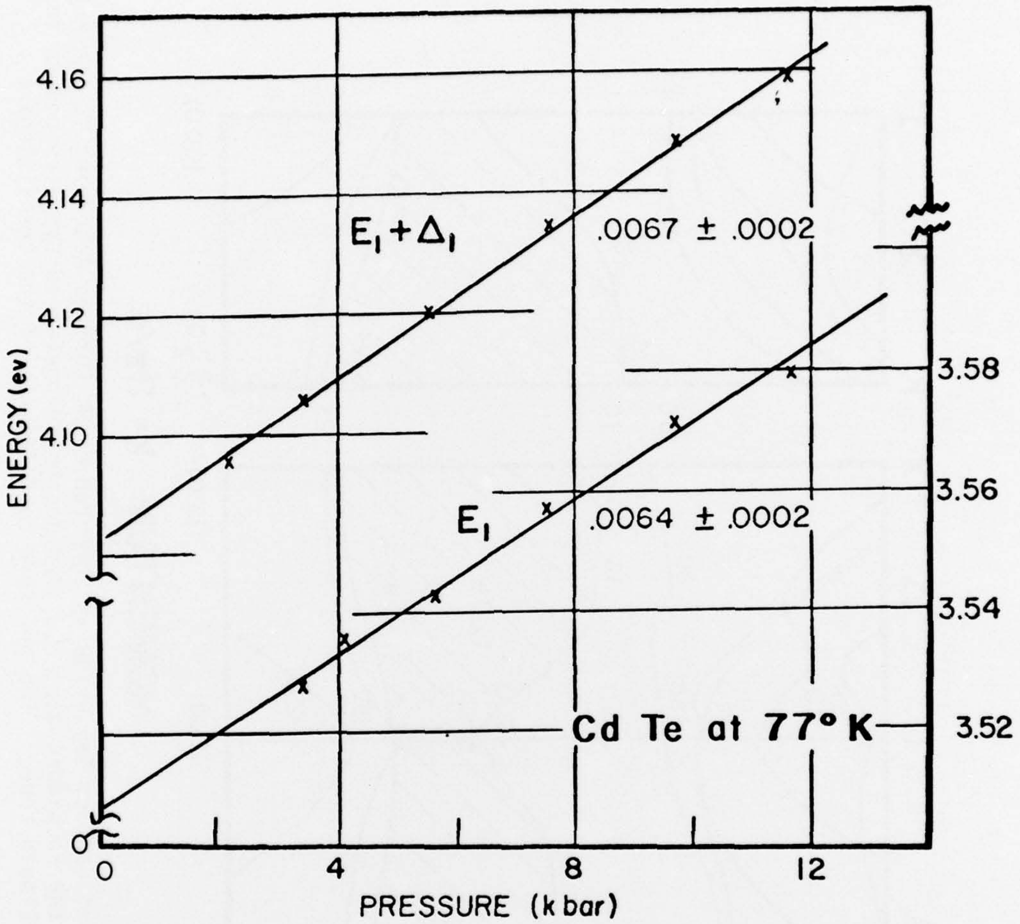

Figure 3. Plotted are the Points of Inflection of the Set of Curves of Figure 1 and Similar Ones Corresponding to the E_1 and $E_1+\Delta_1$ Transition in CdTe. The small scatter of points from a straight line is a measure of the accuracy of the linear coefficient.

TABLE 1

PRESSURE COEFFICIENTS OF BANDGAPS OF II-VI COMPOUNDS

COMPOUND	ENERGY GAP (eV)	k-point	$(dE/dP)_T$ (10^{-6} e V/bar)
CdTe	1.6	Γ	8.0 ± 0.2
	3.4	L	6.4 ± 0.3
	4.0	L	6.7 ± 0.3
ZnTe	2.3	Γ	11.3 ± 0.2
	3.7	L	5.9 ± 0.6
	4.3	L	6.2 ± 0.6
ZnSe	2.8	Γ	10.8 ± 0.4
ZnS	3.7	Γ	6.3 ± 0.2
CdS	2.6	Γ	4.5 ± 0.1
ZnO	3.4	Γ	2.7 ± 0.1

Linear compressibilities and isothermal volume compressibilities have also been determined as listed in Table 2. With the help of these compressibility parameters the valid theories should reproduce the measured pressure shifts of the bandedges. A recalculation with different lattice constants would not imply new complications or adjustable parameters and thus should furnish a true check of the method of calculation. Unfortunately up until now such agreement has not been found quantitatively, but that is not the fault of the experiments.

TABLE 2

COMPRESSIBILITIES OF II-VI COMPOUNDS

COMPOUND	lin. comp. in 10^{-7} bar^{-1})	vol. comp. in 10^{-7} bar^{-1})
CdS $\perp$	5.26	1.568
CdS $\parallel$	5.15	
CdSe $\perp$	6.22	1.823
CdSe $\parallel$	5.79	
CdTe	7.61	2.283
ZnO $\perp$	2.21	6.91
ZnO $\parallel$	2.49	
ZnS	4.24	1.271
ZnSe	4.88	1.463
ZnTe	6.40	1.921

In another example of our work of probing electronic properties of crystals by pressure we first found an experimental disagreement with theory. Consequently we had to implement the theory in order to describe our findings. Finally we succeeded and in turn our implementation showed up consequences for the binding forces of excitons in all large bandgap semiconductors.

Applying uniaxial pressure in directions perpendicular or parallel to the c-axis of wurtzite II-VI compound crystals should shift the energy bands and accordingly the exciton ground states if one follows the conventional deformation potential theory. If the pressure is perpendicular to the c-axis and the propagation direction of light is parallel to the c-axis, the exciton transition energy splits into two components, one completely polarized with $E \parallel P$ and one with $E \perp P$.

These results could be explained only after we added to the usual Hamiltonian, which determines the exciton energies, a term $1/2T\ \sigma_h \cdot \sigma_c$ which represents the spin exchange interaction between electron and hole.

Especially emphasized should be the following two points: 1) Only with the help of these uniaxial pressure measurements could the crystal field parameter, (Δ_1), and the anisotropic spin-orbit parameters, (Δ_2) and (Δ_3), be determined. Without pressure, one always had to rely on a quasi-cubic model to approximate the actual anisotropic case. 2) The size and the effect of the exchange (J) could be determined. Its effect is shown to increase in large bandgap semiconductors. In the case of zincoxide, the energy separation between the three excitons at the point, even at atmospheric pressure, can be shown to be determined as much by the spin orbit interaction as by the exchange interaction ($\Delta_2 \simeq J$), which had previously been completely ignored in ZnO and in all other similar crystals. Table 3 shows the results obtained for ZnO, CdS, and CdSe.

TABLE 3

COEFFICIENTS USED FOR THE "BEST" FIT IN THE Γ_5 MATRIX

		ZnO	CdS	CdSe
Crystal Field	Δ_1	.0268	.0460	.0712
Spin-Orbit	Δ_2	.0074	.0157	.1286
	Δ_3	.0155	.0191	.1424
Exchange	J	.0066	.0022	-.00016
Deformation Potentials	C_1	-.0040	-.00091	-.00078
	C_2	-.0058	-.0041	-.0038
	C_3	-.0010	-.0035	-.0039
	C_4	.0037	.0021	.0023
	C_5	.0014	.0015	.0012

EFFECTIVE G-VALUES IN II-VI COMPOUNDS

Another entity derivable from the specific bandstructure of a compound is the "g-value" of the electrons in conduction and valence band extrema. This value could be considered as a factor determining the splitting of the energy states of an electron which is subjected to a magnetic field. The comparison of this value to the one for a free electron provides a measure for the contribution of the solid crystal on the properties of the electron in the crystal. It can be calculated from bandstructure parameters. However, usually on the basis of assumptions, neglections of certain parameters and approximations. Again, the experimental results are needed to test the validity of these theoretical results and their implications. By themselves they are valuable experimental parameters to describe the magneto-electrooptical behavior of the semiconducting compound.

The method used was based on the determination of the interband Faraday rotation: Monochromatic and polarized light is focused on the sample. When the sample is subjected to a magnetic field, the direction of polarization will be rotated as the light traverses the sample. The degree of this rotation is measured and its dependence on the wavelength of the light furnishes the relevent functional information which is useful for device applications and as a comparison for available theories. A rotational parameter, K (deg/cm.G), independent of the energy of the probing light, can be derived also. Table 4 lists the results obtained for K and the g-values for several II-VI compounds.

TABLE 4

PARAMETER K AND g OBTAINED BY FARADAY ROTATION MEASUREMENTS

COMPOUND	K (10^{-2}deg/cmG)	g effective
ZnS	3.25	2.86
ZnSe	3.36	6.71
CdS	2.54	2.78
ZnTe	4.00	11.1

ELECTRONIC DENSITIES OF STATES

Measurements of the electronic density of states are yet another way to obtain experimental results which can be directly related to the results of bandstructure calculations. Actually the bandstructure calculations provide very detailed information of all allowed energy states of electrons, E, as function of their momentum, k. The density of electronic states is a summation of the allowed energy states over the entire momentum space.

Experimentally the density distribution of occupied electronic states can be obtained by spectroscopic measurements of emitted photoelectrons if the energy of the exciting UV or X-ray radiation is well defined. This method has been adapted by this group for the study of electronic density of state distributions in semiconductors; the electron emission being induced by monochromatic X-rays.

Figure 4 may serve as an example of this type of measurement. The solid line is the experimentally determined density of states distribution, while the calculated one is indicated by the dashed curve. During the past years, densities of valence states were determined for Ge, Si, GaAs, TnAs, TnSb, TnP, ZnSe, ZnTe, HgS, HgSe, HgTe, CdS, CdSe, CdTe, Mg_2Sn, Mg_2Ge, Mg_2Si, PbS, PbSe, PbTe, Se, GeTe and several ternary compounds derived from elements of the first, third and sixth column of the periodic table. For the last mentioned ones there have not been made any theoretical calculations for comparisons. Besides, the electronic core levels of all these compounds were measured, which furnish information about the ionicity of these compounds.

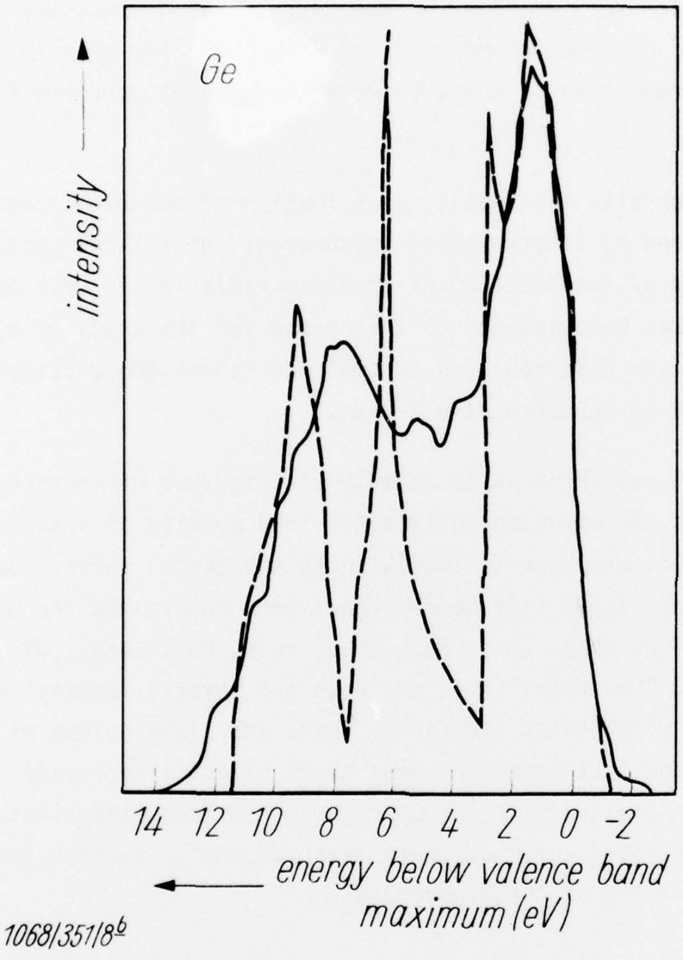

Figure 4. Actual and Calculated Densities of States Distribution

SECTION III

SOME PROPERTIES OF IMPURITIES AND DEFECTS IN II-VI SEMICONDUCTORS

Next to the properties of the basic semiconducting material the potential of this material for certain devices will be governed by the electronic and optical properties of defects of impurities which are willingly or inadevertently added to the host lattice. These effects are partially due to the chemical or physical nature of the defect; thus they can act as donors as acceptors of electrons. Secondly effects can be observed which are due to the interaction of the defect and the surrounding lattice. This interaction can be observed by optical spectroscopy. The following three main areas were investigated in this project:

CRYSTAL FIELD EFFECTS

Impurities which are substituting a regular atom in a crystal are subjected to electric fields from all the neighboring atoms. Certain impurities like Mn in ZnS can be used as probes to measure the magnitude and symmetry of this field.

We have measured, by observation of the Mn^{2+} impurity spectra, the crystal fields in ZnS, and in ZnSe. The relevant parameters in terms of the crystal field theory are $F_2 = 55454$ cm^{-1}, and $F_4 = 34520$ cm^{-1} and Dg = 405 cm^{-1} for ZnSe and $F_2 = 56498$ cm^{-1} and $F_4 = 34485$ cm^{-1} and Dg = 440 cm^{-1} for ZnS. Furthermore we determined the pressure dependence of the crystal field in Al_2O_3 using Cr^{3+} as optical probe and obtained Dg = 1800 cm^{-1} (its preserve coefficient equals 1.05 cm^{-1} $kbar^{-1}$) B = 655 cm^{-1} (pressure coefficient: minus 0.03 $cm^{-1}kbar^{-1}$) and C = 3168 (pressure coefficient: minus 0.35 $cm^{-1}kbar^{-1}$).

PHONON INTERACTIONS

Radiative decay of localized excited states often shows the interaction of lattice vibration with the impurity. The detailed study of the luminescence and photo conductivity -- CdS -- CdSe mixtures and in ZnS: Mn has been used to obtain phonon coupling parameters and also to obtain the spectrum of optically active phonons. For mixed crystals the results could be reasonably well described by a linear chain model. The results further lead to conclusions and an explanation for the observed fact that the lasing threshold for CdS_xSe_{1-x} mixtures is lower as for either CdS or CdSe.

LASING AND ABSORPTION UNDER HIGH EXCITATION

The study of luminescence by exciting the crystals with extremely high power densities (by laser) led to the observation of nonlinear behavior of ZnSe, ZnO, and CdS. A large number of stimulated (lasing) transitions were observed. Their frequency/intensity distribution was found to depend on the power level of the excitation. This effect lead us to the discovery of an "induced absorption" which occurs in normally transparent frequency regions of the crystal. The importance of this effect to laser-induced damage of optical components has been pointed out in a paper presented at the AF Science and Engineering symposium. Several attempts have been made to explain the physical origin of the induced absorption along the lines of two-photon absorption and absorptions due to free carriers or excitons.

APPENDIX

LISTING OF DETAILED RESULTS

1. D. W. Langer, "Pressure Effects on the Bandstructure of II-VI Compound with Zincblende Structure," Proceedings Intern. Conf. Physics of Semiconductors, Paris, (1964) (Dunrod, Paris 1964, p. 242).

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