Two-photon spectroscopy study of ZnS and CdS under hydrostatic pressure

A. Mang, K. Reimann,* St. Rübenacke, and M. Steube
Institut für Physik, Universität Dortmund, 44221 Dortmund, Germany
(Received 18 September 1995)

Two-photon absorption at low temperatures was used to determine the pressure dependence of $2P$ and $1S$ excitons in ZnS and of $2P$ excitons in CdS. From these measurements precise values for the band-gap shifts were obtained. Further, in ZnS pressure-induced changes of the exciton binding energy and of the spherical valence-band parameter (derived from the $2P$ exciton fine structure) were observed. [S0163-1829(96)01624-4]

I. INTRODUCTION

Two-photon spectroscopy[1,2] (TPS) has proven to be a useful tool for the investigation of the electronic band structure of semiconductors under hydrostatic pressure.[3–6] In order to *accurately* determine the band gap and its shift with pressure by optical means, it is necessary to measure exciton energies. In linear absorption this is only possible by using very thin samples (thickness of the order of 1 μm), which are difficult to handle without causing additional strain. In reflection, the quality of the surface is crucial. Because of this, reflection measurements are typically performed on samples cleaved and maintained in vacuum, which is obviously not possible for high-pressure measurements. With TPS, on the other hand, one detects a bulk signal, which is not influenced by the quality of the surface. Often TPS spectra show smaller linewidths than linear absorption spectra. Additionally, because of different selection rules it is possible to excite a larger number of states. As an example, one can measure $2P$ excitons with TPS, which allows the determination of Luttinger parameters[7–11] of the valence band.

There are two main reasons for doing high-pressure experiments. First, the change of the electronic band structure of a semiconductor upon decreasing the lattice constant can be reproduced easily by theoretical calculations. Therefore, hydrostatic pressure allows a direct comparison of theory and experiment. The second reason to perform high-pressure experiments arises from technological applications of direct-gap semiconductors. Especially II-VI compounds as ZnS and CdS have been of interest for the realization of blue-green laser diodes.[12,13] Because of lattice mismatch II-VI quantum wells show strong internal strain, which leads to a change of band structure. For the optimization of optical devices[14] it is important to know the relevant material parameters. Several of them can be determined by hydrostatic-pressure experiments.

The topics of this paper are the direct-gap II-VI semiconductors zinc sulfide (ZnS) and cadmium sulfide (CdS), which both crystallize in a tetrahedrally coordinated structure, ZnS in the cubic zinc-blende structure and CdS in the hexagonal wurtzite structure. In both cases the band gap is direct and at the Γ point. The optical transition between the valence and conduction band is electric-dipole allowed. The lowest conduction band is formed predominantly by s orbitals of the cations, and the uppermost valence bands by sulfur p orbitals with some admixture of zinc or cadmium d orbitals. In the absence of interactions the valence band is sixfold degenerate (including spin degeneracy). Spin-orbit coupling leads to a splitting into an upper fourfold and a lower twofold degenerate band.[15] Their energy difference is called Δ_{so}. The cubic crystal field results in a splitting of the fourfold degenerate valence band into a heavy-hole and a light-hole band for nonzero wave vectors. The form of these bands can be described by the Luttinger parameters[7,8] γ_1, γ_2, and γ_3. In terms of these parameters the heavy- and light-hole masses are given by

$$m_{\mathrm{hh}}=\frac{m_0}{\gamma_1-2\gamma_2},\quad m_{\mathrm{lh}}=\frac{m_0}{\gamma_1+2\gamma_2}, \tag{1}$$

with m_0 the free-electron mass.

In wurtzite, on the other hand, the hexagonal crystal field and spin-orbit coupling together, which in CdS are of the same order of magnitude,[16] lead to three twofold degenerate bands.[17,18] These three valence bands are usually designated[19] in order of decreasing energy A, B, and C.

To understand optical spectra in semiconductors, the Coulomb interaction of electrons and holes has to be taken into account, which leads to the formation of excitons.[20,21] These form hydrogenlike series; i.e., the energy E_n of the exciton with principal quantum number n is given by

$$E_n=E_g-\frac{R}{n^2},\quad n=1,2,3,\ldots\ . \tag{2}$$

Each exciton series is characterized by the band gap E_g, which is also the series limit, and the exciton binding energy R. By the observation of (at least) two excitons with different n it is thus possible to precisely determine the relevant band gap.

Because of the degeneracy of the upper valence band in ZnS, the $2P$ exciton has a fine structure. The underlying mechanism[9] to explain this structure is envelope-hole coupling, i.e., the coupling of the $2P$ envelope function (orbital momentum $l=1$) to the valence band (orbital momentum $j=3/2$). This results in three states, which are classified by the total orbital momentum $F=3/2$, 5/2, and 1/2. Further contributions, which take into account the cubic crystal field, give an additional splitting of the $2P_{5/2}$ state. In the following we restrict ourselves to the spherical approximation ($\gamma_2=\gamma_3$); i.e., we neglect this additional splitting. In this approximation the $2P$ exciton energies are given by[22,23]

 © 1996 The American Physical Society

$$E(2P_{3/2}) = E_{2P} - \mu R/5,$$

$$E(2P_{5/2}) = E_{2P} + \mu R/20, \tag{3}$$

$$E(2P_{1/2}) = E_{2P} + \mu R/4.$$

In these equations μ is the spherical valence-band parameter, which is related to the Luttinger parameters by[9]

$$\mu = \frac{2\gamma_2}{\gamma_1 + \gamma_e}, \tag{4}$$

with γ_e the inverse of the conduction-band mass (in units of the free-electron mass). Thus, μ is proportional to $m_{\mathrm{lh}}^{-1} - m_{\mathrm{hh}}^{-1}$, the difference between the inverse of the light-hole mass and the inverse of the heavy-hole mass [cf. Eq. (1)]. In this way it is possible to determine the pressure dependence of the splitting between heavy- and light-hole bands by measuring the $2P$ exciton fine structure.

II. EXPERIMENT

In the case of ZnS we used a polycrystalline sample, since it had much smaller exciton lines than several single-crystalline samples we tried. A similar observation[5] was also made for ZnSe. A possible explanation is a higher impurity content of the single crystals. The CdS sample used was a single crystal, again selected for the smallest exciton linewidths.

The experimental setup[24] consists of an exciting laser, a cryostat with the sample in a diamond anvil cell, and a detection system. We use only one laser beam; i.e., the excitation is performed with two identical photons. Thus, states are excited at twice the laser photon energy. With regard to one-photon absorption the sample is completely transparent. The exciting laser is a tunable dye laser with a pulse length of 5 ns, which is pumped by the second harmonic of a Nd:YAG (yttrium aluminum garnet) laser with a repetition rate of 10 Hz. Two-photon absorption is detected by the subsequent emission of free-exciton luminescence. The intensity of this luminescence is proportional to the square of the laser intensity, which was around 10 MW/cm^2. The luminescence is separated from the laser light by appropriate optical filters and a prism monochromator and detected by a photomultiplier. The electronic signal from the photomultiplier is fed into a gated integrator, digitized by an analog-digital converter, and sent to a PC, which divides the signal by the square of the laser intensity to compensate for intensity fluctuations and averages the result over 50 to 150 shots. The spectral resolution is twice (because of two-photon absorption) the linewidth of the dye laser, which is 20 μeV.

Pressure is generated by a gasketed diamond anvil cell similar to the one in Ref. 25, but smaller in dimensions to fit into a helium cryostat. Helium is used as pressure medium to ensure optimal hydrostatic conditions at low temperatures. For the measurements the diamond anvil cell is cooled down to a temperature of 7 K in a helium-flow cryostat while changes of pressure are done at room temperature.[26] Pressure is determined by the well-known ruby pressure scale.[27–31]

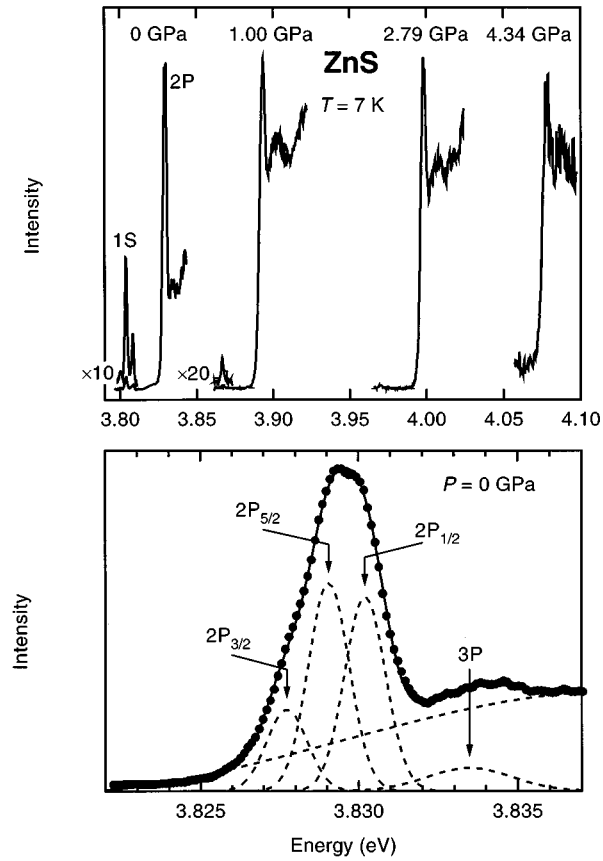

FIG. 1. Above: Two-photon-absorption spectra of the longitudinal $1S$ exciton and the $2P$ exciton in ZnS for different pressures at a temperature of 7 K. Below: Fine structure of the $2P$ exciton in ZnS at zero pressure. The dots are the experimental points and the lines give the deconvolution into the three $2P$ exciton states according to Eq. (3), the $3P$ exciton, and the background due to the exciton continuum.

III. RESULTS AND DISCUSSION

A. ZnS (zinc-blende structure)

Figure 1 shows some spectra of ZnS at different pressures. One finds the resonances of the longitudinal $1S$ exciton and of the $2P$ exciton. In the zero-pressure spectrum there is an additional peak at the high-energy side of the $1S$ exciton from the transverse polariton. With pressure both resonances shift to higher energies. Further, the intensity of the $1S$ exciton decreases relative to the $2P$ exciton. Because of this the $1S$ resonance is below the detection limit for pressures above 3.4 GPa whereas the stronger $2P$ resonance can be detected up to $P = 6$ GPa.

The decrease of the $1S$ exciton intensity relative to the $2P$ exciton is probably caused by a decrease of d admixture to the valence band under pressure since the two-photon oscillator strength of S excitons is proportional to this admixture. A similar decrease of d admixture with pressure was found[3] in CuCl.

Figure 2 gives the energies of $1S$ and $2P$ excitons versus pressure. The pressure dependence of the energies is sublinear and is fitted by quadratic polynoms, given as solid lines in Fig. 2. For both $1S$ and $2P$ excitons the same quadratic pressure coefficient is chosen. With Eq. (2) one can deter-

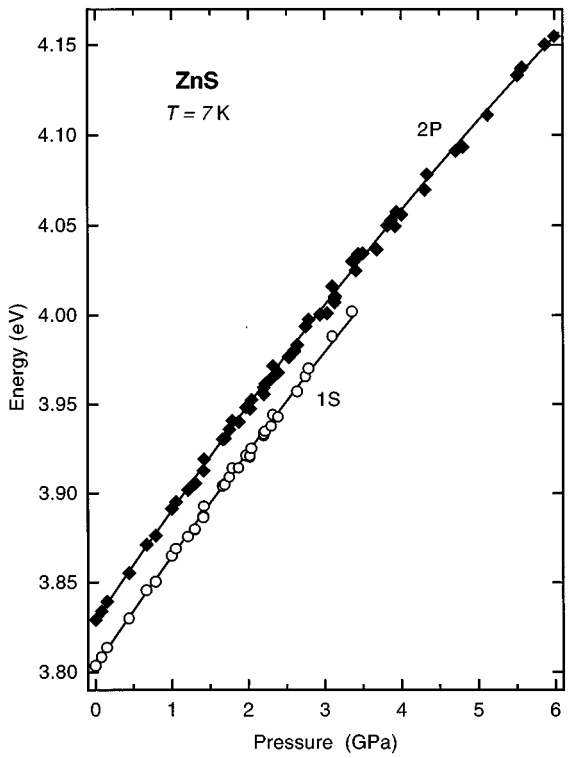

FIG. 2. Energy of the longitudinal 1S exciton and the 2P exciton in ZnS vs pressure at a temperature of 7 K. The solid lines show quadratic fits.

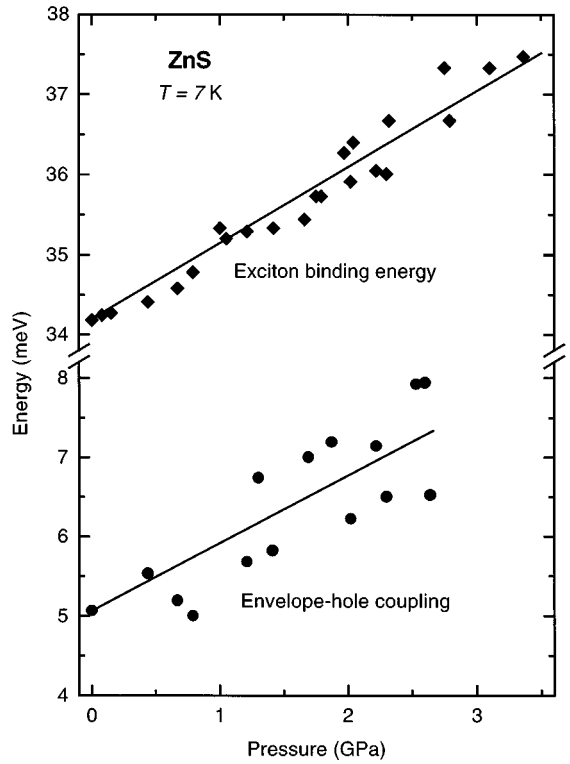

FIG. 3. Exciton binding energy R and envelope-hole coupling μR in ZnS vs pressure. The solid lines show linear fits.

mine the pressure dependence of the band gap E_g and of the exciton binding energy R. Additionally, the envelope-hole coupling μR can be obtained by analyzing the line shape of the 2P exciton[5,10,11] using Eq. (3). The data are shown in Fig. 3 together with linear fits. Table I summarizes all results for ZnS. For comparison Table II gives the results[5] for ZnSe.

The hydrostatic deformation potential a_g describes the volume dependence of the band gap. It can be calculated from the pressure dependence using the bulk modulus B_0:[32]

$$a_g \equiv -\frac{1}{V}\frac{dE_g}{dV} = B_0 \frac{dE_g}{dp}. \tag{5}$$

TABLE I. Zero-pressure values and linear and quadratic pressure coefficients of exciton energies and band parameters in ZnS determined by two-photon absorption at a temperature of 7 K.

	$E(P=0)$ (eV)	dE/dP (meV/GPa)	d^2E/dP^2 (meV/GPa^2)
1S	3.8031±0.0001	63.3±0.6	−1.5±0.1
2P	3.8289±0.0001	63.5±0.4	−1.5±0.1
R	0.0342±0.0001	0.8±0.1	0
E_g	3.8375±0.0001	63.8±0.5	−1.5±0.1
μR	0.0051±0.0001	0.6±0.1	0
	$\mu(P=0)$	$d\mu/dP$ (1/GPa)	
μ	0.149±0.003	0.014±0.003	

As shown in Table III, the deformation potentials for ZnS and ZnSe are very similar; i.e., the difference in their band-gap pressure coefficients is caused mainly by their different bulk moduli (74.8 GPa for ZnS,[33] 64.7 GPa for ZnSe,[34] both for low temperatures).

In the three zinc chalcogenides ZnO, ZnS, and ZnSe the relative change of the exciton binding energy with pressure is larger than the relative change of the band gap (see Table III). In the Wannier model[20,21] the exciton binding energy is given by

$$R = \frac{R_H}{m_0}\frac{m_{\rm red}}{\epsilon_{\rm st}^2}, \tag{6}$$

TABLE II. Zero-pressure values and linear and quadratic pressure coefficients of exciton energies and band parameters in ZnSe determined by two-photon absorption (Ref. 5) at a temperature of 6 K.

	$E(P=0)$ (eV)	dE/dP (meV/GPa)	d^2E/dP^2 (meV/GPa^2)
1S	2.80355±0.00005	69.5±0.2	−1.44±0.02
2P	2.8175±0.0001	69.9±0.2	−1.44±0.02
3P	2.8203±0.0001	70.3±0.3	−1.44±0.02
R	0.0187±0.0001	0.69±0.07	0
E_g	2.8222±0.0001	70.2±0.2	−1.44±0.02
μR	0.00378±0.00004	0.20±0.07	0
	$\mu(P=0)$	$d\mu/dP$ (1/GPa)	
μ	0.202±0.003	0.003±0.004	

TABLE III. Hydrostatic deformation potential a_g and relative changes of band gap E_g and exciton binding energy R with pressure for the wurtzite semiconductors CdS and ZnO (Ref. 4) and for the zinc-blende semiconductors ZnS and ZnSe (Ref. 5).

	a_g (eV)	$\frac{1}{R}\frac{dR}{dP}\left(\frac{1}{\text{GPa}}\right)$	$\frac{1}{dE_g}\frac{dE_g}{dP}\left(\frac{1}{\text{GPa}}\right)$
CdS	2.91±0.05		0.0179±0.0003
ZnO	3.51±0.01	0.0176±0.0003	0.00718±0.00003
ZnS	4.64±0.03	0.023±0.003	0.0166±0.0001
ZnSe	4.54±0.02	0.037±0.004	0.0249±0.0001

with $R_H = 13.6$ eV the Rydberg energy of atomic hydrogen, m_0 the free-electron mass, m_{red} the reduced exciton mass, and ϵ_{st} the static dielectric constant. From $\mathbf{k}\cdot\mathbf{p}$ theory[35] one expects the relative change of m_{red} to be equal to the relative change of E_g. Thus, the observed increase of R cannot be explained completely by the increase of m_{red} with pressure. One expects therefore in all three substances a decrease of ϵ_{st} with pressure. In ZnSe such a decrease was found experimentally.[36]

As already mentioned in the Introduction, the $2P$ exciton fine structure (see Fig. 1) allows the determination of the spherical valence-band parameter μ. Whereas the pressure dependence of band gaps and exciton binding energies is similar in ZnS and ZnSe, the pressure dependence of μ is quite different (see Tables I and II). In ZnS μ increases significantly with pressure, in ZnSe it stays constant. This difference may be due to the influence of the split-off valence band in ZnS, since here the spin-orbit splitting ($\Delta_{\text{so}} = 70$ meV) is much smaller than in ZnSe ($\Delta_{\text{so}} = 430$ meV).[37] An increase of μ means that the difference between heavy- and light-hole masses increases with pressure.

Table IV gives a comparison of our result for the pressure dependence of the band gap of ZnS with previously obtained values. The experimental data, which were obtained by several different methods, all agree within their experimental errors, apart from Ref. 38. One must stress, however, that the present investigation actually determines the band gap and its pressure dependence. Other experiments have measured band-gap-related structures, but, to our knowledge, not the band gap itself. As an example, in the absorption measurements[38,39] the band gap is arbitrarily taken as the energy where the absorption saturates, i.e., where the transmitted light is equal to dark noise plus stray light. Therefore, the band gap determined in this way depends on experimental conditions and on the thickness of the sample, which is the reason for the different results in Refs. 38 and 39. To our knowledge, none of the previous experiments makes a distinction between the band gap and the $1S$ exciton. Accordingly, none of them is able to determine the pressure dependence of the exciton binding energy.

In contrast to the experimental data, the theoretical values show a large variation (between 36 and 86 meV/GPa). The best agreement with experiment is achieved by linear-muffin-tin-orbital (LMTO) calculations.[39,40]

TABLE IV. Experimental and theoretical values for the linear pressure coefficient of the lowest-energy band gap in ZnS.

dE_g/dP (meV/GPa)	Method
Experiment	
63.8±0.5	Two-photon absorption, $T=7$ K, this work
63.5±0.7	Absorption, $T=300$ K, Ref. 39
64 ±2	Luminescence excitation, $T=300$ K, Ref. 45
63 ±2	Reflection, $T=300$ K, Ref. 46
57	Absorption, $T=300$ K, Ref. 38
Theory	
62	LMTO, Ref. 40
79.7	Tight binding, Ref. 47[a]
62.2	LMTO, Ref. 39
86	Pseudopotential, Ref. 48[a]
53	*Ab initio*, Ref. 49[a]
52	Pseudopotential, Ref. 50[a]
36	Pseudopotential, Ref. 51
72	Dielectric theory, Ref. 52
67	Korringa-Kohn-Rostoker, Ref. 53[a]

[a]Calculated with a bulk modulus (Ref. 33) of $B=74.8$ GPa using Eq. (5).

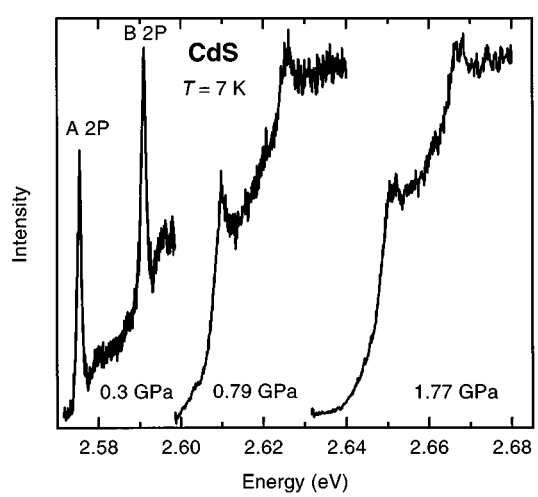

FIG. 4. Two-photon-absorption spectra of the $2P$ excitons from the A and B series in CdS at a temperature of 7 K.

B. CdS (wurtzite structure)

Some two-photon spectra of CdS for different pressures are shown in Fig. 4. One can see two resonances, which are identified as the $2P$ excitons of the A and the B series. Both

TABLE V. Zero-pressure values and linear and quadratic pressure coefficients of the $2P$ exciton energies in CdS determined by two-photon absorption at a temperature of 7 K. Δ_{AB} is the difference between A and B valence band.

	$E(P=0)$ (eV)	dE/dP (meV/GPa)	d^2E/dP^2 (meV/GPa^2)
A $2P$	2.5753±0.0003	46.2±0.8	−1.8±0.1
B $2P$	2.5909±0.0003	46.7±0.8	−1.8±0.1
Δ_{AB}	0.0156±0.0003	0.7±0.3	0

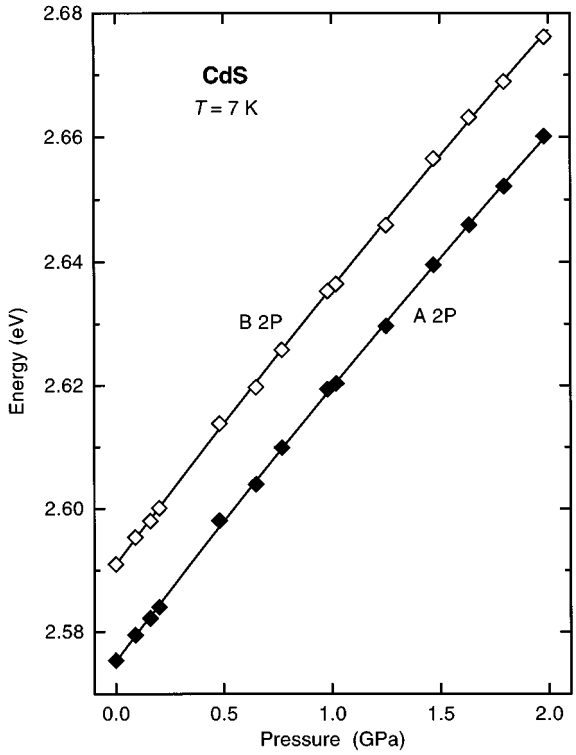

FIG. 5. Energy of the $2P$ excitons (A and B series) in CdS vs pressure at a temperature of 7 K. The solid lines show quadratic fits.

resonances undergo a sublinear blueshift with pressure as shown in Fig. 5. The solid lines are quadratic fits, the results of which are shown in Table V. As in the case of ZnS the quadratic pressure coefficient is chosen to be the same for both excitons. Since we do not observe excitons with principal quantum number $n \neq 2$ in CdS, it is not possible to determine the change of exciton binding energy with pressure. One can, however, assume the pressure shift of the band gaps to be almost equal to the pressure shift of the corresponding $2P$ excitons, since the difference between E_{2P} and E_g is only $R/4$ [Eq. (2)]. In ZnS, for instance, this difference is below the experimental error.

We have used the low-temperature bulk modulus $B = 63$ GPa from Ref. 41 to calculate the hydrostatic deformation potential for CdS with Eq. (5). It is given in Table III. One notes that the deformation potentials for the wurtzite semiconductors CdS and ZnO are considerably smaller than for the zinc-blende compounds ZnS and ZnSe.

The pressure range for the measurements on CdS in the wurtzite phase is limited by a pressure-induced phase transition at $P_c = 2.75$ GPa.[42] Since all pressure changes were done at room temperature, the phase transition took place at this temperature. Upon cooling the pressure decreases. Therefore, at 7 K we could measure the wurtzite phase only up to a pressure of 2 GPa. The high-pressure phase has rock-salt structure and is an indirect-gap semiconductor.[43] We were not able to measure any two-photon signal in this phase.

TABLE VI. Experimental and theoretical values for the linear pressure coefficient of the lowest-energy band gap in CdS.

dE_g/dP (meV/GPa)	Method
Experiment	
46.2±0.8	Two-photon absorption, $T = 7$ K, this work
43 ±3	Absorption, $T = 78$ K, Ref. 44
47 ±3	Absorption, $T = 300$ K, Ref. 44
45.0±0.2	Luminescence, $T = 77$ K, Ref. 54
45.0±0.5	Absorption, $T = 77$ K, Ref. 54
42 ±3	Absorption, $T = 300$ K, Ref. 55
43.6±1.3	Luminescence, $T = 6$ K, Ref. 56
44.7±2.2	Luminescence, $T = 300$ K, Refs. 57
45.5±0.5	Absorption, $T = 300$ K, Ref. 42
33	Absorption, $T = 300$ K, Ref. 38
Theory	
55	Pseudopotential, Ref. 58
61	Dielectric theory, Ref. 52

A comparison of our result for the pressure dependence of the lowest gap with previous results is given in Table VI. Here the same comments as for ZnS apply with the exception of the absorption measurements by Lindner *et al.*[44] They used very thin samples (thickness about 1 μm) and were thus able to measure exciton energies. In principle one could use their $1S$ exciton energies to determine the pressure dependence of exciton binding energies, but the experimental errors are too large for this. In contrast to their finding that Δ_{AB}, the difference between A and B valence band, stays constant with pressure at 15 ± 1 meV, we find an increase of Δ_{AB} with pressure (see Table V).

IV. SUMMARY

We have determined the band-gap deformation potentials of ZnS and CdS at low temperatures with high accuracy by two-photon spectroscopy. In ZnS we have also determined the exciton binding energy and the fine structure of $2P$ excitons. The spherical valence-band parameter μ, which is derived from this fine structure, increases with pressure in contrast to the case of ZnSe, where it stays constant.

ACKNOWLEDGMENTS

We are grateful to Dr. D. Fröhlich for his steady interest and helpful advice and to Dr. K. Syassen (Max-Planck-Institut für Festkörperforschung, Stuttgart) for the generous loan of the high-pressure cell. Financial support was granted by the Deutsche Forschungsgemeinschaft.

*Present address: Department of Physics, University of California at Berkeley, Berkeley, California 94720-7300; Electronic address: reimann@physics.berkeley.edu

[1] D. Fröhlich, in *Festkörperprobleme*, edited by J. Treusch (Vieweg, Braunschweig, 1981), Vol. XXI, p. 363.

[2] D. Fröhlich, in *Nonlinear Spectroscopy of Solids: Advances and Applications*, edited by B. Di Bartolo and B. Bowlby (Plenum, New York, 1994), p. 289.

[3] K. Reimann and St. Rübenacke, Phys. Rev. B **49**, 11 021 (1994).

[4] A. Mang, K. Reimann, and St. Rübenacke, Solid State Com-

mun. **94**, 251 (1995).

[5] A. Mang, K. Reimann, and St. Rübenacke, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors, Vancouver*, edited by D. J. Lockwood (World Scientific, Singapore, 1995), Vol. 1, p. 317.

[6] K. Reimann, St. Rübenacke, and M. Steube, Solid State Commun. **96**, 279 (1995).

[7] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

[8] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, Berlin, 1996).

[9] N. O. Lipari and A. Baldereschi, Phys. Rev. B **6**, 3764 (1972).

[10] M. Sondergeld and R. G. Stafford, Phys. Rev. Lett. **35**, 1529 (1975).

[11] M. Sondergeld, Phys. Status Solidi B **81**, 253 (1977).

[12] M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheng, Appl. Phys. Lett. **59**, 1272 (1991).

[13] H. Luo and J. K. Furdyna, Semicond. Sci. Technol. **10**, 1041 (1995).

[14] A. R. Adams, High Pressure Res. **3**, 43 (1990).

[15] K. Shindo, A. Morita, and H. Kamimura, J. Phys. Soc. Jpn. **20**, 2054 (1965).

[16] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[17] U. Rössler, Phys. Rev. **184**, 733 (1969).

[18] K. Cho, Phys. Rev. B **14**, 4463 (1976).

[19] J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).

[20] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[21] R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

[22] A. Baldereschi and N. O. Lipari, Phys. Rev. Lett. **25**, 373 (1970).

[23] U. Rössler, in *Festkörperprobleme XIX*, edited by J. Treusch (Vieweg, Braunschweig, 1979), p. 77.

[24] F. Beerwerth, D. Fröhlich, P. Köhler, V. Leinweber, and A. Voss, Phys. Rev. B **38**, 4250 (1988).

[25] G. Huber, K. Syassen, and W. B. Holzapfel, Phys. Rev. B **15**, 5123 (1977).

[26] K. Reimann and K. Syassen, Phys. Rev. B **39**, 11 113 (1989).

[27] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[28] D. M. Adams, R. Appleby, and S. K. Sharma, J. Phys. E **9**, 1140 (1976).

[29] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[30] D. D. Ragan, R. Gustavsen, and D. Schiferl, J. Appl. Phys. **72**, 5539 (1992).

[31] J. Yen and M. Nicol, J. Appl. Phys. **72**, 5535 (1992).

[32] G. L. Bir and G. E. Pikus, *Symmetry and Strain-induced Effects in Semiconductors* (John Wiley, New York, 1974).

[33] J. C. Jamieson and H. H. Demarest, Jr., J. Phys. Chem. Solids **41**, 963 (1980).

[34] B. H. Lee, J. Appl. Phys. **41**, 2984 (1970).

[35] E. O. Kane, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 1, p. 75.

[36] G. F. Schötz, E. Griebl, H. Stanzl, T. Reisinger, and W. Gebhardt, Mater. Sci. Forum **182-184**, 271 (1995).

[37] P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).

[38] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids **11**, 140 (1959).

[39] S. Ves, U. Schwarz, N. E. Christensen, K. Syassen, and M. Cardona, Phys. Rev. B **42**, 9113 (1990).

[40] I. Gorczyca and N. E. Christensen, Phys. Rev. B **48**, 17 202 (1993).

[41] I. B. Kobiakov, Solid State Commun. **35**, 305 (1980).

[42] B. Batlogg, A. Jayaraman, J. E. Van Cleve, and R. G. Maines, Phys. Rev. B **27**, 3920 (1983).

[43] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. **25**, 49 (1978).

[44] M. Lindner, S. H. L. Zott, G. F. Schötz, W. Gebhardt, P. Perlin, and P. Wisniewski, High Pressure Res. **10**, 408 (1992).

[45] P. Jaszczyn-Kopec, B. Canny, and G. Syfosse, J. Lumin. **28**, 319 (1983).

[46] D. Langer, in *Physique des Semiconducteurs—Comptes Rendus du 7e Congrès International, Paris*, edited by M. Hulin (Vieweg, Braunschweig, 1964), p. 241.

[47] D. Bertho, D. Boiron, A. Simon, C. Jouanin, and C. Priester, Phys. Rev. B **44**, 6118 (1991).

[48] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).

[49] J. E. Bernhard and A. Zunger, Phys. Rev. B **36**, 3199 (1987).

[50] A. Blacha, H. Presting, and M. Cardona, Phys. Status Solidi B **126**, 11 (1984).

[51] Y. F. Tsay, S. S. Mitra, and B. Bendow, Phys. Rev. B **10**, 1476 (1974).

[52] D. L. Camphausen, G. A. N. Connell, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).

[53] F. Cerdeira, J. S. DeWitt, U. Rössler, and M. Cardona, Phys. Status Solidi **41**, 735 (1970).

[54] X. S. Zhao, J. Schroeder, T. G. Bilodeau, and L. G. Hwa, Phys. Rev. B **40**, 1257 (1989).

[55] A. Béliveau and C. Carlone, Semicond. Sci. Technol. **4**, 277 (1989).

[56] U. Venkateswaran and M. Chandrasekhar, Phys. Rev. B **31**, 1219 (1985).

[57] U. Venkateswaran, M. Chandrasekhar, and H. R. Chandrasekhar, Phys. Rev. B **30**, 3316 (1984); in *Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1984), p. 1117.

[58] K. J. Chang, S. Froyen, and M. L. Cohen, Solid State Commun. **50**, 105 (1984).