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Pressure coefficient of the direct band gap of the solid solution $Zn_xCd_{1-x}S$

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The room-temperature pressure dependence of the direct optical gap (E_g) of $Zn_xCd_{1-x}S$ crystals was measured in a diamond-anvil cell up to their respective pressure-induced phase transition. The typical blue shift of the band edge was observed for every concentration. For CdS, this variation is linear, while a nonlinear increase is measured for ZnS. The linear pressure coefficients, when plotted against the cadmium concentration, display a slow decrease up to 25% at which concentration a sudden drop appears. This behavior is reminiscent of "percolation-type" phenomena.

I. INTRODUCTION

Optical-absorption technique combined with the use of a diamond-anvil high-pressure cell provides a suitable approach to obtain useful information on the pressure dependence of the electronic structure of semiconductors. Although many binary semiconductors have been carefully studied in this regard, very little work has been reported on the semiconducting solid solutions of the type $A_xB_{1-x}C$.

The selection of specific physical properties by the control of the concentration x increases the interest in such mixed semiconductors. Atmospheric pressure characteristic behaviors with composition of such pseudobinary compounds like optical bowing,[1] phase transition,[2] or electronics band crossing[3] are often reported but few studies on the composition dependence of pressure effects are known. Lemos *et al.*[4] analyzed the effect of pressure on the optical bowing of $CdSe_xTe_{1-x}$ and observed no systematic dependence. Goñi *et al.*[5] mentioned that their work on the effect of pressure in $Ga_xIn_{1-x}P$ is consistent with a decrease of the optical bowing under pressure. The work of Lifshitz *et al.*[6] showed an anomalous behavior of the linear pressure coefficient with concentration for $Al_xGa_{1-x}As$. A special interest has been given to the optical properties of the semimagnetic mixed semiconductors $Cd_xMn_{1-x}Te$ (Ref. 7) and $Zn_xMn_{1-x}Te$.[8]

Most of these solid solutions go through either a phase transition or a band crossing with composition which limit the range x of interest. The mixed crystals $Zn_xCd_{1-x}S$ grow in the wurtzite phase for $0 \leq x \leq 0.9$ and, characteristic of the II-VI family, do not present any band crossing, therefore extending the interesting range of composition. This solid solution is a technologically interesting material, because it has shown great potential for use in photovoltaic cells.[9]

The parent binary compounds of this series have been intensively studied. The first investigation on the effect of pressure on the optical-absorption edge of CdS was done by Grusche[10] who observed a linear increase of the band gap with pressure. Later, Edwards and Drickamer[11] also observed this linear variation and found an abrupt red shift at about 27 kbar which they attributed to a first-order phase transition. These behaviors have been well studied since.[12-14] For the other binary compound of this series, ZnS, previous experiments[15,16] have only observed a linear increase of the band gap with pressure, though clear nonlinear behaviors are reported for the similar compounds ZnSe (Ref. 17) and ZnTe.[18]

In this work, we report the pressure dependence of the optical band gap of the mixed crystals $Zn_xCd_{1-x}S$. We observe for the first time a nonlinear variation of the direct band gap of ZnS. We also investigate the behavior of the linear pressure coefficients with composition and observe a sharp change at some critical concentration.

II. EXPERIMENTAL TECHNIQUES

The $Zn_xCd_{1-x}S$ crystals were grown for the full range $0 \leq x \leq 1.0$ by chemical transport using iodine as a transporter. We analyzed their structure using x-ray powder diffraction and as was previously observed,[19] these crystals are of the wurtzite structure except for composition $x \geq 90\%$ where the zinc-blende structure becomes dominant. The zinc concentration was derived from the measured lattice constants using Vegard's law with an estimated uncertainty of $\Delta x = \pm 0.02$.

Optical-absorption measurements were obtained as a function of pressure at room temperature using the diamond-anvil cell. The crystals were mechanically polished with the c axis perpendicular to the plane with typical thicknesses being about 30 μm. Such thicknesses are sufficiently small for absorption measurements in these crystals since the absorption edge is attributed to a direct band transition and no indirect transition masks the direct absorption profile. The optical setup is described elsewhere[20] and a Xe arc lamp was used as a light source. Since these crystals vary considerably in color (dark orange for CdS and transparent for ZnS), their energy gap ranges from visible to the uv and therefore the spectra were obtained on two different systems: on a SPEX Industries, Inc. 1-meter monochromator for the uv region and on a Jarrel-Ash 1-meter monochromator for the visible range.

To minimize the scattered light background in the high-pressure cell, especially in the uv region, an internal optical mask was used. This setup consisted of a 100-μm-thick compressed gasket which was composed of a 300-μm-diam, 80-μm-deep high-pressure chamber followed by a 100-μm-diam, 20-μm-deep aperture. It has proven useful in reducing considerably the background noise[21] and is gaining popularity in high-pressure optical-absorption measurements.[13] A 4:1 mixture of methanol:ethanol was used as a pressure transmitting medium and the usual ruby fluorescence technique allowed us to measure the pressure.

The absorption coefficient α was obtained from $d^{-1}\ln(I_0/I)$ and was not corrected for reflection. This induces a nonvanishing value for this coefficient in the transmitting region of the crystal. Since we are in the presence of a direct band gap, one ideally has $\alpha \propto (\hbar\omega - E_g)^{1/2}$ for the incident photon energy greater than the gap ($\hbar\omega \geq E_g$) and $\alpha = 0$ otherwise. Realistically, for measurements at room temperature, one must include finite lifetime effects; this can be done through a Lorentz broadening Γ and we write[22]

$$\alpha = \frac{K}{(\hbar\omega)} \left[\frac{\Gamma}{2} \right]^{1/2} [E + (E^2+1)^{1/2}]^{1/2} + C \tag{1}$$

where $E = (\hbar\omega - E_g)/\Gamma$, K is a constant, and C is added to take into account the nonvanishing part of the absorption due to the neglect of reflectivity.

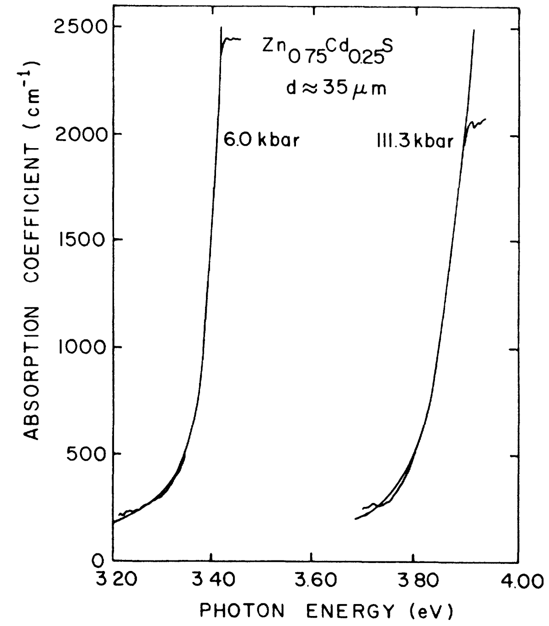

FIG. 1. The absorption coefficient for the crystal $Zn_{0.75}Cd_{0.25}S$. The thickness of the sample was ~ 35 μm. The wiggly curves are experimental and the solid curves are obtained from a least-squares fit of Eq. (1). The parameters used in the model are $K = 5.61 \times 10^4$ cm^{-1}(eV)$^{+1/2}$, $E_g = 3.397$ eV, $\Gamma = 1.848 \times 10^{-2}$ eV, and $C = -189.6$ cm^{-1} for the curve obtained at 6 kbar and $K = 4.915 \times 10^4$ cm^{-1}(eV)$^{+1/2}$, $E_g = 3.869$ eV, $\Gamma = 3.565 \times 10^{-2}$ eV, and $C = -361.8$ cm^{-1} for that at 111.3 kbar.

Though the optical band edge is due to direct exciton absorption,[12] we obtained the band-gap energy by a least-squares fit of our measured spectra to this corrected expression for the direct electronic transition. For high-pressure measurements, this approach yields results similar to the usual saturation point technique[5,8] and is far less subjective. In both approaches, an error in the absolute value of E_g^0 is introduced but precise measurements of the pressure variation of the band gap are achievable. Figure 1 shows the results generated by a least-squares fit to Eq. (1) for the crystal $Zn_{0.75}Cd_{0.25}S$ for two pressures.

III. RESULTS AND DISCUSSION

We have measured the variation of the direct band gap under pressure for seven different concentrations x (0, 0.16, 0.33, 0.58, 0.75, 0.87, 1.0) of $Zn_xCd_{1-x}S$ up to their respective phase transition. The transition brings the crystals into a new phase (rocksalt structure[12,15]) which is opaque to visible light and its absorption edge for pressure higher than the transition pressure could not be measured by our apparatus.

For every concentration x, we observed a blue shift of the direct band gap with pressure. We represent in Fig. 2 the absorption coefficient as a function of the incident photon energy for the binary compound ZnS at different pressures. We believe the variation of the absorption edge structure for pressure above 120 kbar could reflect the solidification of the pressure transmitting fluid[23] but such a deformation in the sudden rise of the absorption is also typical of this family of compounds when they approach their phase transition.[8]

For most semiconductors, the variation of the direct band gap under pressure can be well described by a quadratic expression of the form

$$E_g(P) = E_g^0 + aP + bP^2 . \tag{2}$$

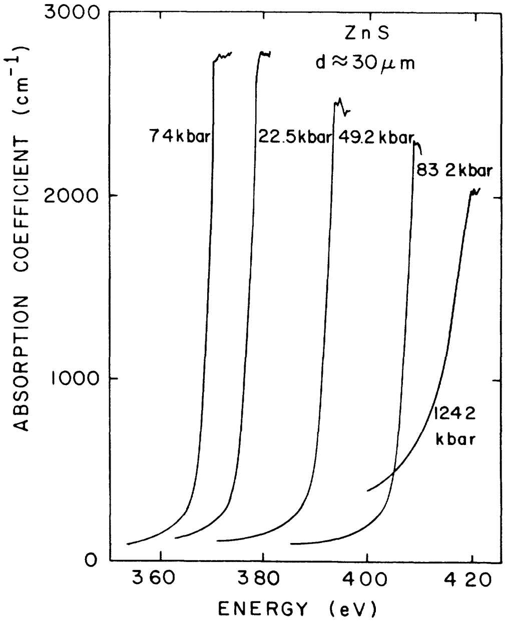

FIG. 2. The absorption coefficient for ZnS at various pressures.

TABLE I. Results for the coefficients obtained from a least-squares fit (up to the phase transition) to $E_g(p)=E_g^0+Ap+Bp^2$ for the family of mixed crystals $Zn_xCd_{1-x}S$.

	x	E_g^0 (eV)	A (meV/kbar)	B (10^{-3} meV/kbar^2)
CdS	0	2.377(2)	4.2(2)	
	0.16	2.524(4)	4.9(4)	−21(7)
	0.33	2.726(2)	5.1(2)	−22(3)
	0.58	3.054(2)	5.2(2)	−15(3)
	0.75	3.360(3)	6.2(2)	−16(3)
	0.87	3.562(3)	6.4(2)	−18(4)
ZnS	1.00	3.641(2)	6.7(2)	−20(4)

Table I gives the results of the least-squares fit of our data to such a polynomial while Fig. 3 shows this variation up to the phase transition for all the studied crystals.

The linear variation of the band gap for CdS yields a value of 4.2 meV/kbar which is situated between the result of Edwards and Drickamer[11] (3.3 meV/kbar) and those of Grusche[10] (4.4 meV/kbar) and of Batlogg *et al.*[12] (4.55 meV/kbar). For the other binary compound, we bring into evidence the expected sublinear variation of the absorption edge of ZnS as a function of pressure; $E_{\text{gap}}(P)-E_0=6.7(2)P-20(4)P^2$. Such a sublinear variation has been observed in ZnSe (Ref. 17) and in ZnTe (Ref. 18) and is in agreement with theoretical calculation.[24] The linear coefficient a ($=6.7$ meV/kbar) is in agreement with the value of 6.5 meV/kbar stated by Camphausen *et al.*[16] but differs from the result of Edwards *et al.*[25] ($a=5.7$ meV/kbar).

For the mixed ternary compounds, the linear pressure coefficients decrease smoothly from a cadmium composition varying between 0 and ~25%, then decrease sharply and remain almost constant until about 75% of cadmium where another (less well-defined) change in slope is observed. The data presented in Fig. 4 bring out this discontinuity, the solid lines are used to enhance those trends. Similar discontinuities have been observed in these crystals when studying their electrical conductivity.[26]

It has been noted[6] that for III-V binary semiconductors with the same anion, the linear pressure coefficient varies inversely with the direct energy gap and therefore is expected to vary smoothly with composition for mixed III-V crystals with a common anion. The same could be expected for II-VI semiconductors. But Lifshitz *et al.*[6] have observed that for $Al_xGa_{1-x}As$, this is not the case. Their study of the pressure coefficients for the direct band gap was restricted to $0 \le x \le 0.5$ due to the Γ-X band crossover, but they noted that a sharp change in these coefficients occurs for concentrations around 0.25–0.30. A similar change is here observed in $Zn_xCd_{1-x}S$ at the same critical concentration $(1-x)\approx 0.25$. No clear understanding of this behavior is available, but Lifshitz *et al.*[6] suggested that percolation might have some role to play.

The observed linear coefficients $a(x)$ reflect an important change in the pressure dependence in the bands at the Γ point upon alloying. It seems that at the critical concentration, the orbitals (most likely the d orbitals since those have shown to be related to the linear pressure coefficient[16]) of cadmium suddenly play an impor-

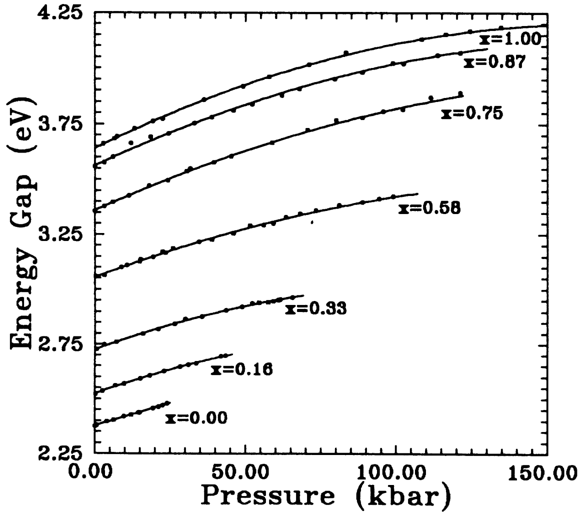

FIG. 3. The pressure dependence of the direct gap of the mixed crystals $Zn_xCd_{1-x}S$, up to the pressure at which a change of phase occurs.

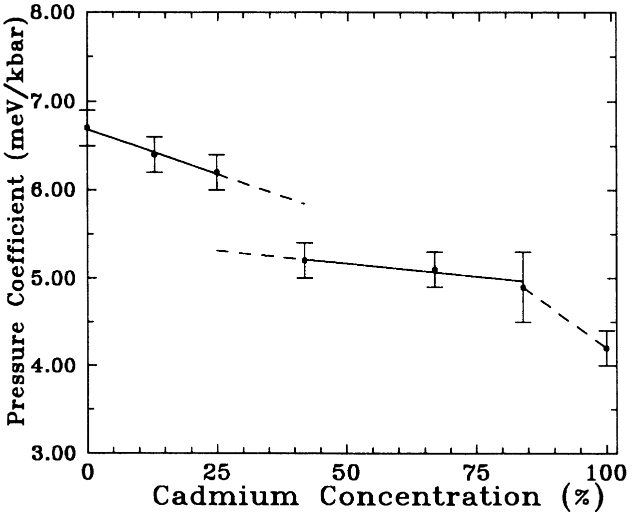

FIG. 4. Linear pressure coefficient of the direct band gap in $Zn_xCd_{1-x}S$ as a function of the cadmium concentration.

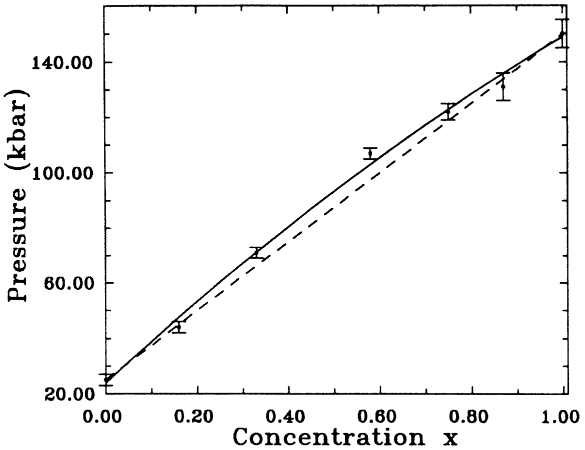

FIG. 5. Compositional dependence of the transition pressure in $Zn_xCd_{1-x}S$. The transition pressure where determined as the pressure at which the crystal becomes optically opaque. The solid line represents a least-squares fit to a quadratic form, while the dashed line is the linear variation between the end compounds.

tant role in the band structure. Though this role does not seem to be affecting the relative separation at the Γ point (since the band gap varies smoothly with composition), the weaker pressure dependence of CdS somehow induced this sharp drop in $a(x)$. This could imply a similar behavior for the compressibility; unfortunately, the compressibility of such crystals has not been measured and we postpone a more detailed discussion until further experimental as well as theoretical investigations are available. Nevertheless, this sudden change of the linear pressure coefficient at some critical concentration is reminiscent of "percolation-type" phenomena.[27]

We are led to propose that the pressure behavior of such solid solutions is controlled mainly by the characteristic of the Zn (or Cd) atom until a critical concentration is reached. If this is the case, the critical pressure P_t inducing a phase transition in these crystals should behave differently in those ranges. Our results for the variation of P_t with concentration do not support this speculation, but nevertheless clearly show a nonlinear variation (see Fig. 5).

IV. SUMMARY AND CONCLUSION

Optical-absorption measurements of $Zn_xCd_{1-x}S$ crystals under high hydrostatic pressure have been reported up to their respective phase transition. The direct band edge increases with pressure for every concentration. The expected nonlinear variation of the band gap for Zns is observed, while the linear increase for CdS is confirmed.

The compositional dependence of the linear pressure coefficient does not show a smooth variation but displays a sharp structure at a concentration of 25% of cadmium. We note that this sudden change is reminiscent of a percolation-type phenomena which could be related to the d orbitals of the cations. Our experimental results should bring interest in the theoretical calculation of the effect of pressure on the band structure of mixed semiconductors and its relation, if any, to percolation phenomena.

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