PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Pressure dependence of shallow acceptors in $CuGa(S_xSe_{1-x})_2$ alloys

J. Gonzalez and E. Calderon
Centro de Estudios de Semiconductores, Facultad de Ciencias, Universidad de Los Andes, Merida 5251, Venezuela

F. Capet and F. Baert
Laboratoire de Dynamique et Structure des Matériaux Moléculaires, UFR de Physique, Université de Lille I,
59655 Villeneuve d'Ascq, France

(Received 13 February 1998; revised manuscript received 6 July 1998)

The effects of hydrostatic pressure on the binding energies of shallow acceptors in $CuGa(S_xSe_{1-x})_2$ are presented and discussed. The energy E_A decreases with pressure at a rate of -4.6×10^{-4} eV GPa^{-1} for $x=1$ and -9.2×10^{-4} eV GPa^{-1} for $x=0.5$. These results can be understood in terms of effective-mass theory, because shallow levels are dominated by long-range forces which are much less sensitive to the interatomic separation (pressure). [S0163-1829(98)06243-2]

I. INTRODUCTION

The quaternary chalcopyrite alloys are very promising materials for photovoltaic applications. This is mainly because these alloys offer a wide range of energy-band gaps and lattice constant parameters which can lead to the utilization of tandem cell structures.[1] The system $CuGa(S_xSe_{1-x})_2$, which shows a single-phase solid solution over the whole composition range and a continuous variation of structure and electronic properties,[2] has received considerable attention.

The fundamental absorption edge of these compounds at low temperatures,[3] as well as a function of both temperature[4] and pressure,[5] has been reported in the literature. It is also well established that excitons play an important role in determining optical properties at low temperature.[4] Since electrical measurements can determine only the most active shallow defect state parameters, information about the defect levels in I-III-VI_2 compounds has been obtained mainly from photoluminescence measurements.[6] However, in such measurements it is not easy to identify the different transitions, and for this reason discrepancies exist in the literature about the nature and origin of these levels.

Although pressure studies of the bulk properties of semiconductors are extensive and have contributed substantially to our understanding of this class of materials, relatively little pressure work has been done on impurity and defect states of this class of materials. Shallow-donor levels in semiconductors of groups IV, III-V, and II-VI are generally well understood,[7] and their properties are satisfactorily described within the framework of effective-mass theory. Comparisons of the pressure dependences of deep and shallow levels can provide interesting physical insights. In fact, the magnitude of the pressure dependence of the binding energy of a level is an excellent means of distinguishing between shallow and deep levels.[8,9]

For the shallow acceptors in semiconductors of the cubic groups IV, III-V, and II-VI, the situation is complicated by the complex nature of the valence band, leading to the presence of both light and heavy holes. This makes the interpretation of the pressure dependence of the ionization energy less certain. However, the triple degeneracy of the p-like Γ_{15} valence band in zinc-blende compounds is completely lifted in chalcopyrite materials under the simultaneous influences of spin-orbit interaction and the uniaxial crystalline field; hence the binding energy of the shallow acceptors are only affected by the heavy-hole valence band.

Therefore, in the present work, we report on the optical absorption study near the band gap of the $CuGa(S_xSe_{1-x})_2$ alloys as a function of pressure up to 15 GPa at 300 K. From the analysis of the results, by using a model which allows us to identify the acceptor states, the pressure dependence of the binding energies of the acceptors levels were obtained. For the shallow acceptors, the pressure derivatives of the binding energies are over an order of magnitude smaller than those of the energy gap.[5] These results can be understood in terms of effective-mass theory.

II. EXPERIMENT

$CuGa(S_xSe_{1-x})_2$ samples were grown by the chemical-vapor transport method, as described elsewhere.[4] The x-ray analysis of Debye-Sherrer powder photographs indicates the presence of a single phase with the chalcopyrite structure ($I42d$). All these samples, as observed by thermal probe, were p type conducting.

The samples used were prepared by mechanical lapping and polishing on both sides of the platelets and later broken into small pieces of the required dimensions for the pressure chamber (transverse dimensions of about 150 μm). In order to determine as precisely as possible the thickness of the samples, two independent procedures were used. In the first procedure, a scanning electron microscope (Itachi S-2500) was used. With this technique, the thickness of a sample could be measured with a precision of ~1%. In the present experiment, the thickness of the sample was 20 μm±1%. Another method is to determine the thickness from the first-order interference pattern obtained by means of the well-known relation $2nd=k\lambda$, where d is the thickness of the sample, λ the wavelength of the interference maximum of order k, and n the refractive index at λ. For the calculation, values of n as a function of wavelength reported in Ref. 10

were used. In this way, the thickness of a sample was measured ($d = 20 \pm 2$ μm).

Optical-absorption measurements were performed in a gasketed diamond-anvil cell (DAC) with a 4:1 methanol-ethanol mixture as the hydrostatic pressure medium. This mixture retains fluidity up to 10 GPa. The pressure was determined to within ±0.1 GPa by using the R_1 line shift of a 10-μm ruby chip placed close to the sample.[11] The maximum pressure gradient across the gasket hole was less than 0.1 GPa, as checked by measuring the pressure distribution with several ruby chips.

The transmittance $T = I/I_0$ was measured by the sample-in–sample-out method, I is the intensity transmitted through the sample, and I_0 the light from the quartz-iodine tungsten lamp, which is measured through the pressure-transmitting medium in the cell, near the sample, by moving the DAC perpendicularly to the beam. In order to prevent errors due to light diffusion in the cell, we used a two-pinhole system. The first one is used to make a small light spot in the cell ($\varnothing \approx 30$ μm). The second one, placed between the cell and the spectrometer, ensures that only light coming directly from the central part of the spot area is analyzed. This method reduces stray light (T_{min}) down to 8.0×10^{-4}.

At low energy, far below the absorption edge of the sample, a nonzero and constant value for the apparent absorption coefficient is found. This is a general case in optical measurements on transparent crystal samples, and comes about for various reasons: imperfections of the crystal, diffusion at the interfaces, etc. In the low-frequency region, where the samples are known to be transparent, the apparent transmittance is corrected by a constant factor a to fit the theoretical transmittance for $\alpha = 0$. This factor is experimentally determined for each pressure and sample by measuring the low-energy constant transmittance region.

The nonpolarized transmitted light was analyzed by a simple Spex monochromator (0.22 m) yielding a linear dispersion of 1 nm mm^{-1} in the first order. The second-order radiation diffracted from the 1200-lines mm^{-1} grating was eliminated by using adequate filters. The radiation was detected by a photomultiplier whose signal was processed with a photon counting system.

Representative transmission spectra of $CuGaS_2$ measured at 2.5 GPa is shown in Fig. 1. This is a typical transmission spectrum of a semiconductor with parallel surfaces which forms an interference cavity where light is reflected at each surface many times. These multiple reflections yield Fabry-Perot (FP) fringes in either transmitted or reflected light. In the low energy region, the FP interference pattern is clearly observed and disappear at about 2.52 eV due to the interband absorption edge.

Finally, the absorption coefficient α is calculated from the transmittance in the absence of interference fringes, and is given by

$$\frac{I}{I_0} = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \tag{1}$$

if $\alpha d \gg 1$; then

$$T = \frac{I}{I_0} \approx (1-R)^2 e^{-\alpha d} \tag{2}$$

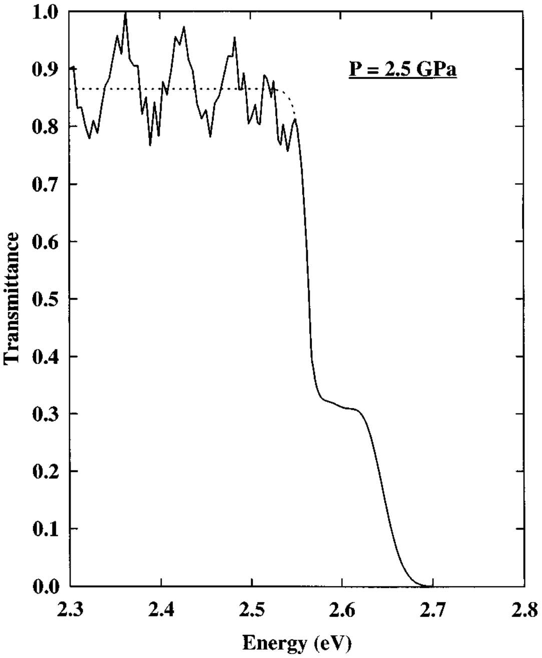

FIG. 1. Solid line: Representative transmission spectra of $CuGaS_2$ at 2.5 GPa. The FP interference pattern is clearly observed. Dashed line: the apparent transmittance value used to calculate the factor a to fit the theoretical transmittance for $\alpha = 0$.

and

$$\alpha = \frac{1}{d}\{2\ln(1-R) - \ln[a(T - T_{\mathrm{min}})]\}, \tag{3}$$

with

$$R = \left[\frac{n - n_0}{n + n_0}\right]^2,$$

where n is the refractive index of the sample, n_0 the refractive index of the methanol-ethanol pressure-transmitting medium, T the experimental transmittance, a the correction factor, and d the thickness of the sample. It should be noted that the correction due to the stray light (T_{min}) has been taken into account in the high-energy, low-transmittance region. The refractive index of methanol-ethanol $n_0(P)$ has been extrapolated from the results of Ref. 12 with the Clausius-Mossotti law.

For the calculation, values of n at 300 K as a function of wavelength, reported in Ref. 10, were used. For the pressure dependence of the refractive index we used the values reported in Ref. 13, calculated from the first-order interference pattern obtained at room temperature. Final errors in the absorption coefficient α due to errors in the determination of the refractive index of methanol-ethanol and the sample and in the experimental transmittance are less than 2% for 100 cm^{-1}$<\alpha<$2500 cm^{-1}; these limits were set by the thickness of the sample.

III. RESULTS AND DISCUSSION

Absorption spectra of $CuGaS_2$ and CuGaSSe at different pressures are shown in Figs. 2 and 3, respectively. An additional shoulder near the fundamental absorption edge

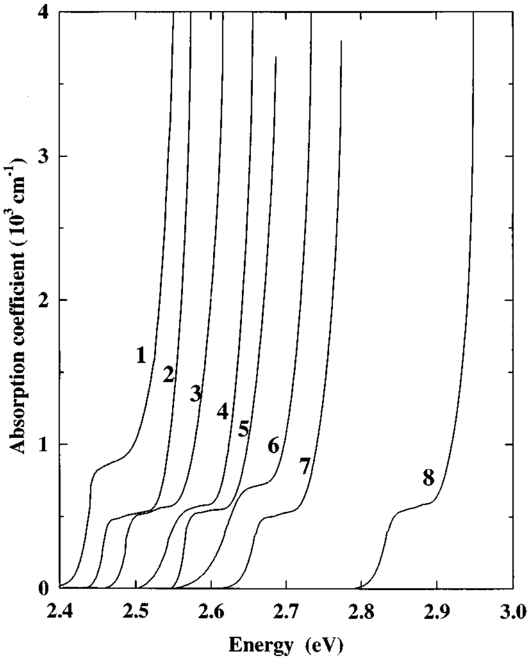

FIG. 2. Shift in the absorption edge with hydrostatic pressure for CuGaS$_2$ ($x=1$). (1) $P=0.0$ GPa. (2) $P=0.2$ GPa. (3) $P=1.0$ GPa. (4) $P=1.9$ GPa. (5) $P=2.5$ GPa. (6) $P=3.7$ GPa. (7) $P=4.5$ GPa. (8) $P=8.8$ GPa.

can be observed in the curves. This residual absorption observed near the fundamental absorption edge at energies below the exciton absorption is probably related to transitions between shallow acceptor or donor levels and the bands. These transitions occur at a photon energy which is given by $h\nu \geqslant E_g - E_I$, where E_I is the binding energy of the impurity. Unlike the exciton absorption which occurs between the well-defined edge of the valence band and a discrete level, the transition between a defect level and the band involves the whole band of levels. Hence such a transition should manifest itself as a shoulder in the absorption spectra having a threshold lower than the energy gap by an amount of E_I.[14]

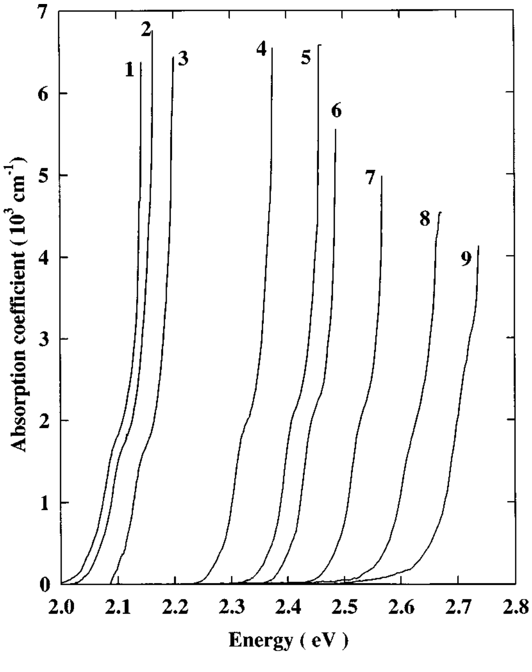

FIG. 3. Shift in the absorption edge with hydrostatic pressure for CuGaSSe. (1) $P=0.3$ GPa. (2) $P=0.6$ GPa. (3) $P=1.1$ GPa. (4) $P=5.0$ GPa. (5) $P=6.8$ GPa. (6) $P=8.0$ GPa. (7) $P=10.1$ GPa. (8) $P=12.8$ GPa. (9) $P=15.7$ GPa.

The various intensities of the absorption due to the shallow levels observed in Figs. 2 and 3, respectively, are caused by two effects: (i) Because the diameter of the light in the sample is about 25 μm, it is generally very difficult to be sure that measurements at each pressure were done in the same region of the sample. (ii) Even if the cell and the microscope objective are moved by the *XYZ* translation stage until a good focus is obtained under pressure, this parameter is very critical and may change the intensity of the light transmitted through the sample.

Assuming, in the case of a direct-gap semiconductor with parabolic bands, that the defect states are shallow, discrete, and nonoverlapping, the absorption coefficient for the acceptor-state-to-conduction-band transition is given by[15]

$$\alpha(h\nu)=\frac{C(h\nu-E_I)^{1/2}}{h\nu\left[1+\frac{m_e^*}{m_h^*E_A}(h\nu-E_I)\right]^4}, \tag{4}$$

where $E_I=E_g-E_A$, E_A is the acceptor binding energy, m_e^* and m_h^* are the effective masses for the electrons and holes, respectively, and C is a constant nearly independent of energy. For the valence-band-to-donor-state transition, one obtains[15]

$$\alpha(h\nu)=D(h\nu-E_I)^{1/2}\sum_{i=\mathrm{lh,hh}}\frac{(m_i/m_0)^{3/2}}{\left[1+\frac{m_i}{m_0E_D}(h\nu-E_I)\right]^4} \tag{5}$$

where $E_I=E_g-E_D$, E_D is the donor binding energy, the sum is taken over the light (lh) and heavy (hh) holes, and D is a constant, again nearly independent of $h\nu$.

The acceptor and donor concentrations of the sample can be estimated from the values of the constants C and D according to the relations[15]

$$C=512\pi e h\nu\langle P\rangle^2(N_A-P_A)/ncm_0^2(m_hE_A/m_0)^{3/2}, \tag{6}$$

$$D=256\pi e^2h\nu\langle P\rangle^2\langle N_D-n_D\rangle/ncm_0^2(m_eE_D/m_0)^{3/2}, \tag{7}$$

where n is the refractive index, c is the vacuum velocity of light, and N_A-P_A and N_D-n_D are the numbers of unfilled acceptors and donors, respectively. $\langle P\rangle$ is the average interband matrix element of the momentum operator.

The absorption linewidth between transitions involving acceptors calculated by using Eq. (4) give a broad absorption band, whereas those involving donors [Eq. (5)] correspond to sharp-line spectra. This effect is meanly related to the electron effective mass in the direct-gap compounds, which is generally smaller than the hole mass, giving a relatively large curvature to the conduction band and a relatively small extend in k (wave vector) to the donor state.

Therefore, the experimental impurity absorption was fitted at each pressure by using Eq. (4), with C, E_I, and $m_e^*/m_h^*E_A$ as adjustable parameters. The pressure depen-

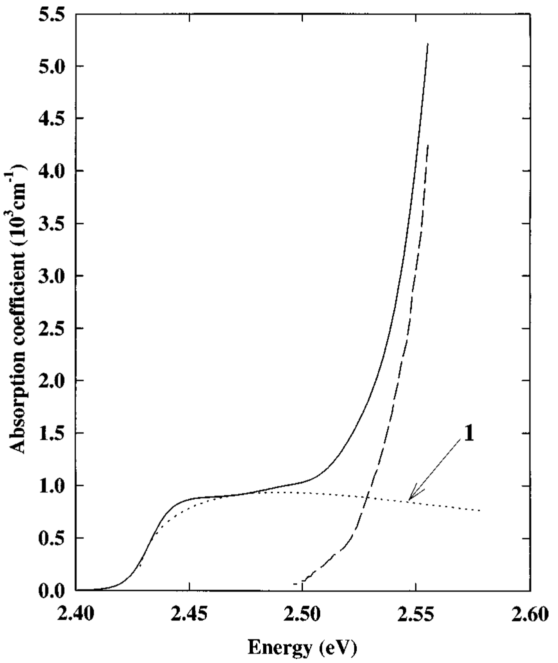

FIG. 4. Spectral dependence of the acceptor to conduction-band transition (curve 1) for $x=1$.

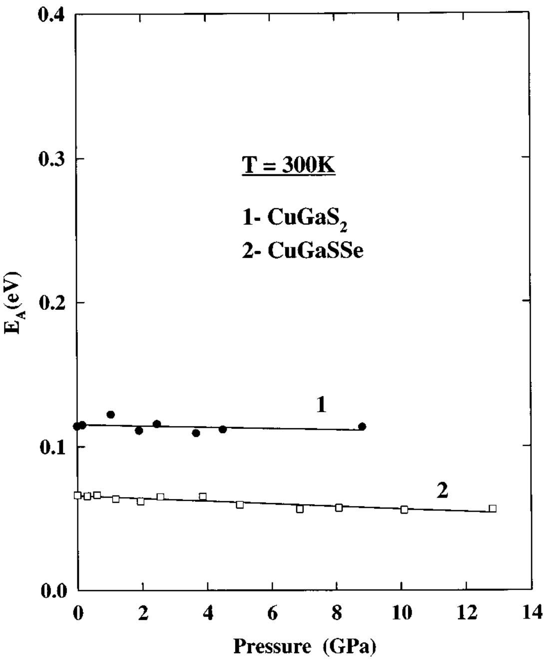

FIG. 5. Pressure dependence of the binding energy of the shallow acceptor for CuGa$(S_xSe_{1-x})_2$ samples.

dence of the energy gap was published previously in Ref. 5, and is reported in Table I. For illustrative purposes, in Fig. 4 we plot separately the theoretical curves related to the acceptor-level-to-band transition (curve 1) for $CuGaS_2$ at $P=0$. The resulting pressure dependence of the binding energies of shallow acceptors are presented in Fig. 5 for $CuGaS_2$ and CuGaSSe. A least-squares fit to the experimental data gives

$$E_A(P)=E_{A0}-bP, \tag{8}$$

where $E_{A0}=1.15\times10^{-1}$ eV and $b=4.6\times10^{-4}$ eV GPa^{-1} for $CuGaS_2$, and $E_{A0}=6.54\times10^{-2}$ eV and $b=9.25\times10^{-4}$ eV GPa^{-1} for CuGaSSe.

In the case of $CuGaS_2$ the acceptor ionization energy $E_A=115$ meV obtained at normal pressure is in good agreement with those values obtained from the electrical properties,[16] luminescence,[6] and optical absorption at low temperature.[4] The chemistry of intrinsic defects in ternary Cu-III-VI_2 compounds has been discussed by several authors, and it has been suggested that the copper vacancy (V_{Cu}) appears as the common acceptor.[4,6,16] As observed from Eq. (8), we can definitely state that E_A decreases with pressure, i.e., the acceptor level moves slightly closer to the valence band, with pressure coefficients which are over an order of magnitude smaller than those of the energy gap.[5] Thus these levels remain essentially pinned to the nearest band edges, as expected from the effective-mass theory.[7] Shallow, hydrogen-like impurity levels show a decrease in activation energy with an increase of acceptor concentration (N_A). With an acceptor-type impurity, the decrease should vary as[16]

$$E_A=E_{A_0}-\beta N_A^{1/3}, \tag{9}$$

where E_{A_0} is the activation energy at the dilute limit of acceptor concentration, and β was estimated to be 2.4×10^{-8} eV cm for $CuGaS_2$.[16] The value of E_{A_0} can be calculated by using the hydrogenic model

$$E_{A_0}=13.6(m_h^*/m_0)/\varepsilon_0^2, \tag{10}$$

where m_h^* is the effective mass of the heavy holes, and ε_0 is the static dielectric constant. Therefore combining Eqs. (9)

TABLE I. Parameters used to fit Eqs. (11), (12), and (13) in $CuGaS_2$ and CuGaSSe.

	Eg (eV)	dEg/dP ($\times10^{-2}$ eV GPa^{-1})	E_A (eV)	B_0 (GPa)	B_0^1	V(0) ($\times10^{-24}$ cm^3)	ε_0	$d\varepsilon_0/dP$ (GPa^{-1})	m_h^*/m_0	n_A ($\times10^{-4}$)
$CuGaS_2$	2.5[a]	4.5[a]	0.115[b]	87.6[c]	3.1[c]	300.09[c]	8.22[d]	−0.061[c]	0.69[e]	3.344[b]
CuGaSSe	2.1[a]	5.1[a]	0.065[b]	79.5[f]	4[f]	321.9[f]	9.25[f]	−0.064[f]	0.647[f]	11.737[b]

[a] Reference 5.
[b] This work.
[c] Reference 13 and 17.
[d] Reference 18.
[e] Reference 16.
[f] Reference 19.

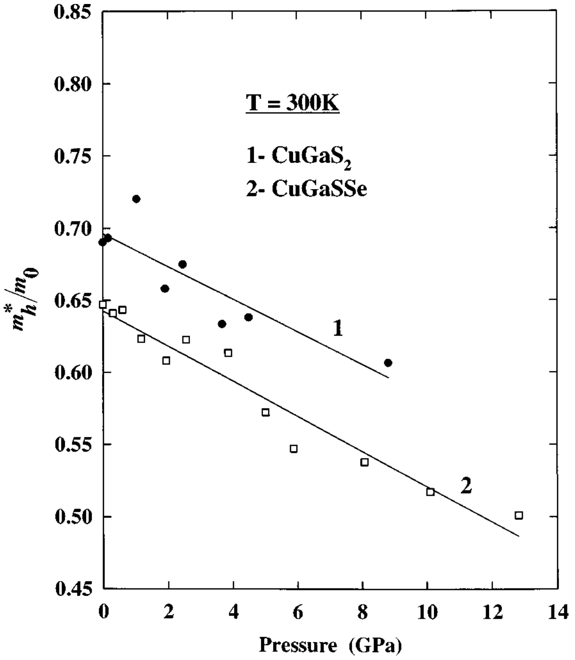

FIG. 6. Pressure dependence of the hole effective mass for CuGa(S_xSe_{1-x})$_2$ samples.

and (10) and using $N_A = n_A/V$, where n_A is the number of the acceptor impurities and V the volume of the unit cell, we obtain

$$E_A = 13.6(m_h^*/m_0)/\varepsilon_0^2 - \beta\left(\frac{n_A}{V}\right)^{1/3}. \tag{11}$$

The value of n_A at normal pressure is calculated using relation (11) with the values of E_A, m_h^*, ε_0, and V. Typical values are given in Table I for CuGaS$_2$ and CuGaSSe, respectively. From Eq. (11), the pressure dependence of E_A can thus be understood in terms of the changes in m_h^*, ε_0, and V. The experimental value of the pressure coefficient of the dielectric constant is reported in Ref. 13 and tabulated in Table I, and that of E_A is given in Eq. (8). The pressure dependence of V is given by the Murnaghan equation of state

$$V(P) = V_0\left(1 + \frac{B_0'}{B_0}P\right)^{-1/B_0'}, \tag{12}$$

where B_0 is the bulk modulus and B_0' is the derivative of B_0 at $P=0$. Experimental values of B_0 and B_0' obtained by *in situ* x-ray measurements under pressure[13,17] are given in Table I. Thus, we can evaluate the pressure dependence of m_h^* according to

$$\frac{m_h^*(P)}{m_0} = \frac{\varepsilon_0^2}{13.6}\left[E_A + \beta\left(\frac{n_A}{V}\right)^{1/3}\right]. \tag{13}$$

The resulting pressure dependences of the hole effective mass are presented in Fig. 6 for CuGaS$_2$ and CuGaSSe, respectively. A least-squares fit to the experimental data gives

$$m_h^*(P) = m_h^*(0) - \alpha P, \tag{14}$$

where $m_h^*(0) = 0.696$ and $\alpha = 0.012$ GPa^{-1} for CuGaS$_2$ and $m_h^*(0) = 0.642$ and $\alpha = 0.013$ GPa^{-1} for CuGaSSe.

The obtained values for the derivatives of the hole effective-mass under pressure for CuGaS$_2$ and CuGaSSe, respectively, are in agreement with the values reported in Ref. 7.

In either case, it is seen that the decrease of E_A with pressure for the CuGaS$_2$ and CuGaSSe samples are dominated by the pressure dependence (decrease) of m_h^*. The decrease in ε_0 with pressure leads to an increase in E_A, but this effect is more than counterbalanced by the pressure dependence of m_h^* and (n_A/V).

In the case of the CuGaSe$_2$ samples ($x=0$), we do not observe the residual absorption near the fundamental absorption edge. It has been reported in the literature that the binding energy of the shallow acceptor (V_{Cu}) in CuGaSe$_2$ is of the order of 30–40 meV.[6] Therefore, at 300 K this level is almost ionized, and contributes to the broadening of the absorption edge.

IV. CONCLUDING REMARKS

In this work we have presented the effects of pressure on a shallow acceptor level in CuGaS$_2$ and CuGaSSe. From the results, the pressure dependence of the binding energies of the acceptors are presented and discussed. The obtained values are over an order to magnitude smaller than those of the pressure dependence of the energy gap. These results can be understood in terms of effective-mass theory.

ACKNOWLEDGMENTS

This work was supported by CONICIT-BID under Grant No. NM-09 and by EEC Grant No. ERBCI1*CT940031, Brussels, Belgium. One of us (J.G.) is grateful to the CDCHT of the Universidad de Los Andes, the CEFI-PCP Materials (France), and CONICIT (Venezuela) for financial support.

---

[1] See, for example, Proceedings of the 9th International Conference on Ternary and Multinary Compounds, edited by H. Kukimoto [Jpn. J. Appl. Phys. **32**, 10 (1993)].

[2] R. G. Goodchild, J. C. Woolley, and J. Gonzalez, Jpn. J. Appl. Phys., Suppl. **19**, 176 (1980).

[3] L. Roa, C. Rincon, J. Gonzalez, and M. Quintero, J. Phys. Chem. Solids **51**, 551 (1990).

[4] C. Bellabarba, J. Gonzalez, and C. Rincon, Phys. Rev. B **53**, 7792 (1996).

[5] J. Gonzalez, E. Calderon, and F. Capet, Phys. Status Solidi B **187**, 149 (1995).

[6] G. Masse, J. Appl. Phys. **68**, 2206 (1990).

[7] G. A. Samara and C. E. Barnes, Phys. Rev. B **35**, 7575 (1987).

[8] W. Jantsch, K. Wünstell, O. Kumagai, and P. Vogl, Phys. Rev. B **25**, 5515 (1982).

[9] M. G. Holland and W. Paul, Phys. Rev. **128**, 30 (1962).

[10] G. D. Boyd, H. Kasper, and J. H. McFee, IEEE J. Quantum Electron. **7**, 563 (1971).

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

[12] M. Gauthier, A. Polian, J. M. Besson, and A. Chevy, Phys. Rev. B **40**, 3837 (1989).

[13] F. Capet, Ph.D. thesis, Université de Lille, 1995.

[14] Y. Toyozawa, Prog. Theor. Phys. **20**, 53 (1958); **27**, 89 (1962).

[15] W. P. Dumke, Phys. Rev. **132**, 1998 (1963).

[16] P. W. Yu, D. L. Downing, and Y. S. Park, J. Appl. Phys. **45**, 5283 (1974).

[17] J. Gonzalez, E. Calderon, T. Tinoco, J. P. Itie, A. Polian, and E. Moya, J. Phys. Chem. Solids **56**, 507 (1995).

[18] J. Baars and W. Koschel, Solid State Commun. **11**, 1513 (1972).

[19] E. Calderon, Master's thesis, Universidad de Los Andes, 1996.