

# Pressure dependence of defects and $p$ - $d$ hybridization in chalcopyrite semiconductors

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We have studied the effect of pressure on optical transitions involving defects in the photoluminescence spectra of two chalcopyrite semiconductors  $\text{AgGaS}_2$  and  $\text{CuGaS}_2$ . In the former compound results obtained in samples doped with either Cd or Au are compared with unintentionally doped samples. In both compounds we find transitions whose pressure coefficients are *larger* than that of the band gap. We have identified these transitions as involving deep acceptors. We propose that in the chalcopyrite semiconductors the valence-band edge can be *less* pressure dependent than the deep acceptors because of  $p$ - $d$  hybridization in the valence-band wave functions. [S0163-1829(97)01515-4]

## INTRODUCTION

Semiconductors with the chalcopyrite structure have been used in devices such as nonlinear optical crystals, detectors, and solar cells.<sup>1-7</sup> Defects in these materials can have deleterious effects on most of their applications and hence their properties have been investigated in a number of previous studies.<sup>8-12</sup> However, the nature of these defects, whether they are shallow or deep, is not known in general. In semiconductors with diamond and zinc-blende structures, it has been shown that shallow and deep defects can be distinguished by their different pressure dependence.<sup>13,14</sup> In this paper we investigate the pressure dependence of defects in bulk single crystals of  $\text{AgGaS}_2$  and  $\text{CuGaS}_2$  via their emission spectra. These crystals are either unintentionally doped or, in the case of  $\text{AgGaS}_2$ , doped with Cd or Au. We found that both materials exhibit emission peaks that have larger pressure coefficients than the band gap. We explain this behavior by the presence of  $p$ - $d$  hybridization in the valence bands of those chalcopyrite semiconductors containing transition-metal cations.<sup>15</sup>

## EXPERIMENTAL DETAILS

$\text{AgGaS}_2$  and  $\text{CuGaS}_2$  bulk single crystals have been grown by the horizontal Bridgman method using a tubular two-zone furnace. Details of the crystal growth process have been described before<sup>8</sup> and will not be repeated here. The as-grown crystals typically show variation in color from one end to the other presumably because of the different amounts and the nature of defects in them. Slices of samples were cut from parts of the ingot and characterized by x-ray diffraction, photoluminescence, and chemical analysis. Selected slices of  $\text{AgGaS}_2$  crystal were doped with Cd or Au. In cases of doping by Au, the sample surface was polished and then a thin film of Au was sputtered onto the surface. It is then annealed at 700 °C for 48 h. Afterwards the sample was polished again to remove any Au remaining on the sample surface. The Cd doping was carried out by putting the sample and Cd

in a fused quartz tube, which is placed in a tubular furnace such that the Cd and  $\text{AgGaS}_2$  samples are maintained at 300 and 400 °C, respectively. High-purity Ar gas was made to flow through the tube at atmospheric pressure to carry the Cd vapor to the  $\text{AgGaS}_2$  sample where the Cd diffused in readily. After about 1 h the Cd is removed from the tube while the  $\text{AgGaS}_2$  sample was maintained at the same temperature in the Ar atmosphere for another hour to drive in the Cd. Thin slices of both doped and undoped samples containing the  $c$  axis were lapped down to a thickness of about 30  $\mu\text{m}$  and polished with Syton. Pressure-dependent measurements are carried out with a diamond anvil high-pressure cell using a methanol/ethanol mixture as the pressure medium. The optical setup has also been described elsewhere and will not be repeated here.<sup>8</sup>

## EXPERIMENTAL RESULTS

### A. $\text{AgGaS}_2$

Figure 1 shows the low-temperature photoluminescence (PL) spectra of five  $\text{AgGaS}_2$  samples labeled as AGS#412 (sample color is yellow), AGS#504 (dark yellow), AGS#510 (light yellow), AGS:Cd (yellow), and AGS:Au (yellow). The first three samples are not intentionally doped while the last two samples have been doped with Cd and Au, respectively. Previous studies have established the energy of free excitons in  $\text{AgGaS}_2$  to be around 2.7 eV.<sup>8</sup> Except for sample AGS#510 the PL spectra of all other samples are dominated by strong broad emission peaks at energies much lower than the excitonic energy. Some of these peaks (such as the one labeled as  $B'$  in AGS#412) have been attributed to donor-acceptor pair recombination. Sample AGS#510, however, shows mainly one relatively sharp peak located near the free exciton energy. The transverse exciton peak energy of 2.700 eV is in excellent agreement with previous reports.<sup>8</sup> One interesting phenomenon in this sample is the quenching of the defect-related emission after several minutes of exposure to laser light. After this quenching the PL spectrum is dominated by the free excitonic peak and a weaker emission in the

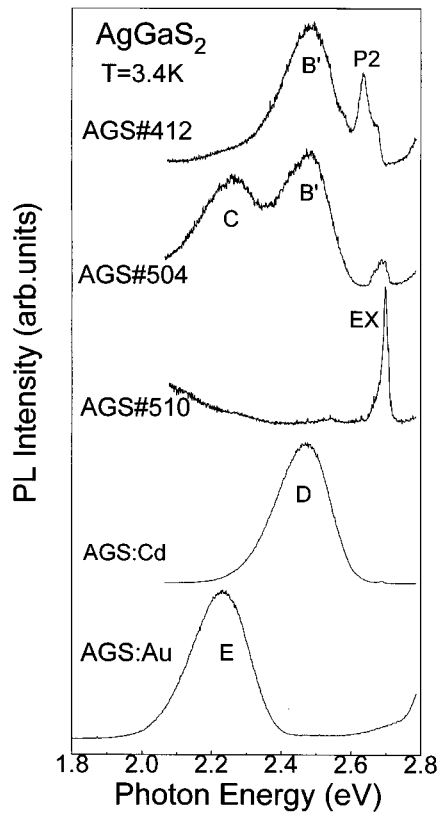


FIG. 1. Low-temperature photoluminescence (PL) spectra of five  $\text{AgGaS}_2$  samples labeled as AGS#412, AGS#504, AGS#510, AGS:Cd, and AGS:Au.

red (a hint of this emission is visible in the low-energy side of the spectrum in Fig. 1). Doping sample AGS#510 with Cd and Au replaces the excitonic peak with strong broad emission peaks ( $D$  and  $E$ ) that are qualitatively similar to the donor-acceptor pair recombination peaks ( $B'$  and  $C$ ) found in samples AGS#504 and AGS#412.

When the sample temperature  $T$  is increased, the PL peaks (labeled  $D$  and  $E$ ) in the doped samples show activated behavior (see Fig. 2). In this figure the circles are experimental results while the curves represent theoretical fits to the data with the expression

$$I_{\text{PL}}(T) = I_0 [1 + C e^{-E_a/k_B T}]^{-1}, \quad (1)$$

where  $I_0$  and  $C$  are adjustable constants,  $E_a$  is an activation energy, and  $k_B$  is the Boltzmann constant. The values of the activation energies obtained from these fits are 29 and 54 meV, respectively, for peaks  $D$  and  $E$  in the Cd- and Au-doped samples.

The pressure-dependent PL spectra of sample AGS:Cd are shown in Fig. 3. Compared to the atmospheric pressure spectrum, additional peaks (labeled  $A$  and  $A'$ ) are found to appear under high pressure. As pressure raises the exciton energy above the excitation laser photon energy, intrinsic absorption is suppressed while extrinsic absorption becomes enhanced, making weaker defect-related emissions observable. The pressure dependence of the three structures  $A$ ,  $A'$ , and  $D$  identified in the sample AGS:Cd are summarized in Fig. 4 (solid triangles and circles). For comparison we show also the pressure dependence (straight lines) of the exciton

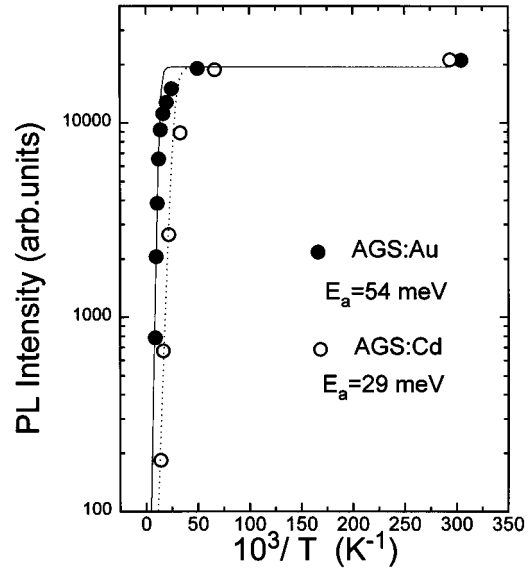


FIG. 2. Arrhenius plots of the emission peaks  $D$  and  $E$  in samples AGS:Cd and AGS:Au, respectively. The solid and dotted curves are fits to the data points with Eq. (1). The activation energies  $E_a$  obtained from these fits are indicated in the figure.

(EX) and donor-acceptor pair emission peaks  $B$  and  $B'$  in sample AGS#412 reported previously.<sup>15</sup> The PL spectra in the sample AGS:Au at several pressures are shown in Fig. 5. In this sample the peak labeled  $E$  dominates at atmospheric pressure and no new structures appear under high pressure.

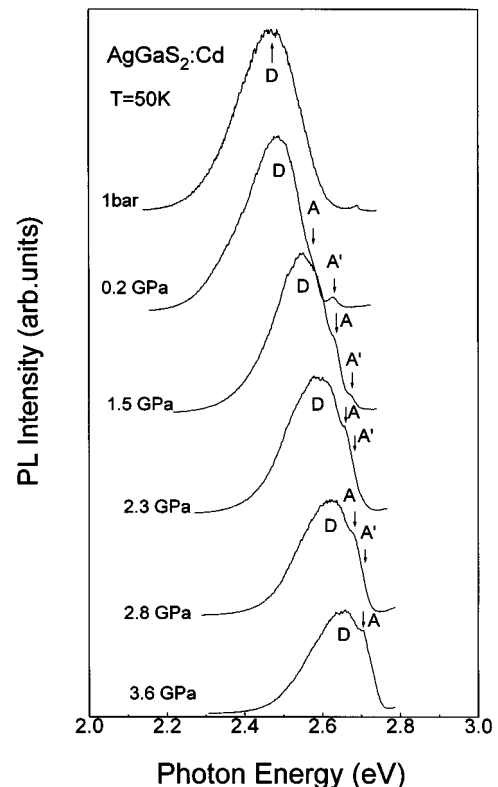


FIG. 3. The emission spectra of the Cd-doped  $\text{AgGaS}_2$  sample AGS:Cd at several applied pressures. The arrows labeled the structures discussed in the text.

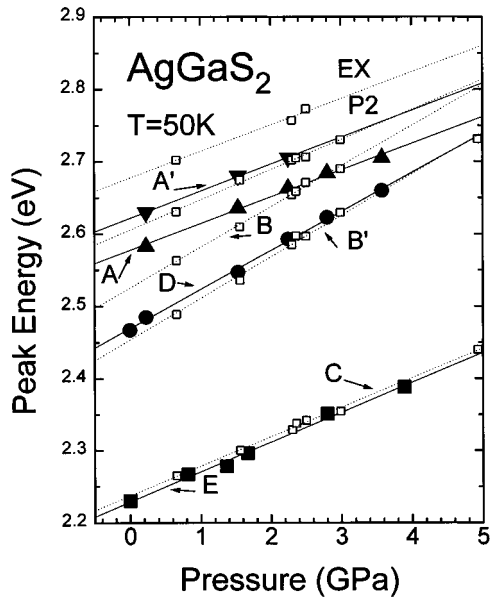


FIG. 4. The energies of the structures identified in sample AGS: Cd (solid points labeled as *A*, *A'*, and *D*) and sample AGS: Au (solid points labeled as *E*) plotted as a function of pressure. The solid lines are least-square linear fits to these data points. The pressure coefficients and standard deviations deduced from these fits are listed in Table I. The open squares (labeled as EX, P2, B, B', and C) represent the pressure dependence of peaks identified in sample AGS#412 reported in Ref. 8. The corresponding least-square linear fits to these data points are represented by the broken lines.

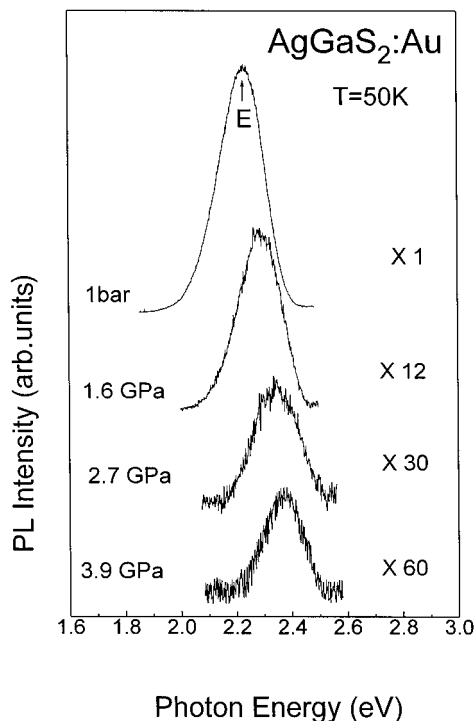


FIG. 5. The emission spectra of the Au doped AgGaS<sub>2</sub> sample AGS: Au at several applied pressures.

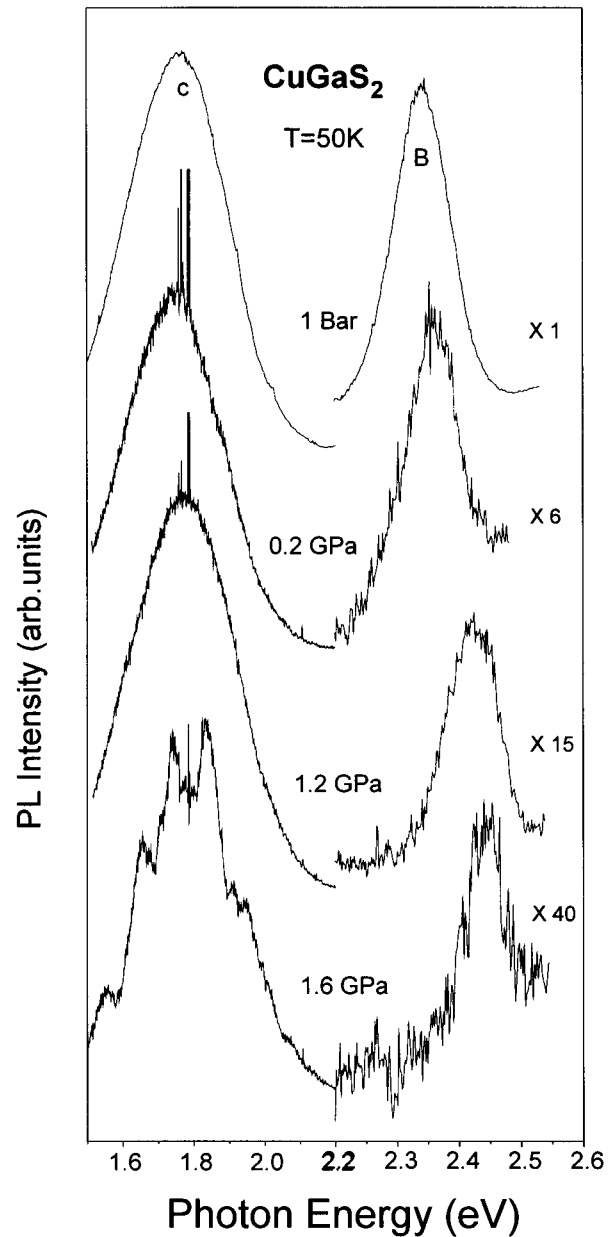


FIG. 6. The emission spectra of the undoped CuGaS<sub>2</sub> sample at several applied pressures.

However, the intensity of this peak decreases strongly as pressure is increased. The pressure dependence of its peak energy is plotted in Fig. 4 as solid squares.

### B. CuGaS<sub>2</sub>

We have reported already in Ref. 15 the pressure dependence of the absorption spectra in unintentionally doped CuGaS<sub>2</sub> samples. In Fig. 6 we present the pressure dependence of the PL spectra in CuGaS<sub>2</sub> samples cut from the same ingot. The emission intensity of the two peaks labeled *B* and *C* decreases rapidly with pressure so that measurements above 1.6 GPa become very difficult. Their peak energies are plotted versus pressure in Fig. 7. For comparison the pressure dependence of the band gap ( $E_g$ ) and exciton (EX) reported in Ref. 15 are plotted in the same figure as broken lines.

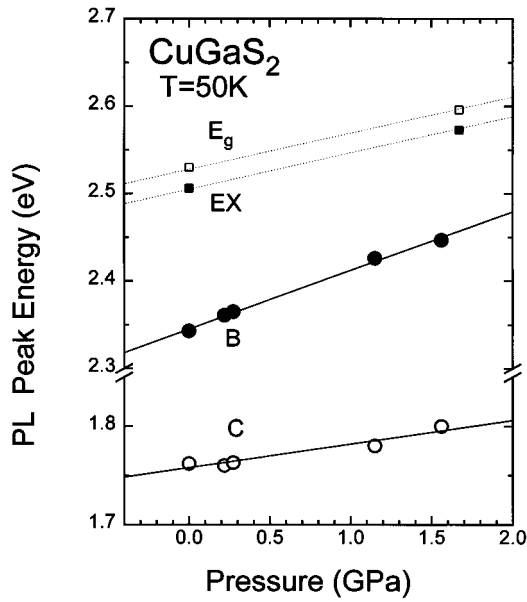


FIG. 7. The pressure dependence of the emission peaks  $B$  (solid circles) and  $C$  (open circles) in the  $\text{CuGaS}_2$  sample as a function of pressure. The solid lines drawn through the data points are least-square fits with a straight line. The pressure coefficients deduced from these fits are listed in Table I. The corresponding pressure dependence of the band gap ( $E_g$ ) and exciton (EX) of  $\text{CuGaS}_2$  measured at 50 K (from Ref. 8) are shown as broken lines passing the open and solid squares, respectively.

The pressure coefficients of the observed emission peaks in both  $\text{AgGaS}_2$  and  $\text{CuGaS}_2$  samples determined by fitting the data points in Figs. 4 and 8 with straight lines are summarized in Table I where they are compared with the results of previous measurements<sup>15,16</sup> including results in  $\text{AgGaSe}_2$ .

## DISCUSSIONS

The activation energies of various defects in both  $\text{AgGaS}_2$  and  $\text{CuGaS}_2$  have been studied extensively via PL and transport measurements. Shallow (or hydrogenic) donor binding energies of about 15–25 meV and acceptor energies of about 100 meV have been reported in  $\text{AgGaS}_2$  by various authors.<sup>10,11</sup> Deep donors of binding energies of 40 and 50 meV have also been mentioned.<sup>11</sup> A very deep center with a binding energy of 0.69 eV has been associated with red emission around 1.8 eV by Yu and Park.<sup>10</sup> The basis for the characterization of these centers in  $\text{AgGaS}_2$  as shallow or deep seems to be have been mainly their binding energies. The exciton binding energy in  $\text{AgGaS}_2$  has been measured precisely by two-photon absorption spectroscopy to be 29 meV.<sup>17</sup> This suggests a shallow donor binding energy of similar magnitude. In the case of  $\text{CuGaS}_2$ , Shirakata, Murakami, and Isomura<sup>18</sup> have estimated the binding energies of its shallow donors and acceptors to be 49 and 130 meV, respectively.

We have reported already the existence of defect-related emission or absorption peaks in  $\text{AgGaSe}_2$  (Ref. 16) and  $\text{AgGaS}_2$  (Ref. 15) whose pressure coefficients are *larger* than that of the band gap and free exciton. We have identified these defects as deep centers. However, the exact nature of these deep centers remains unknown. In the present experi-

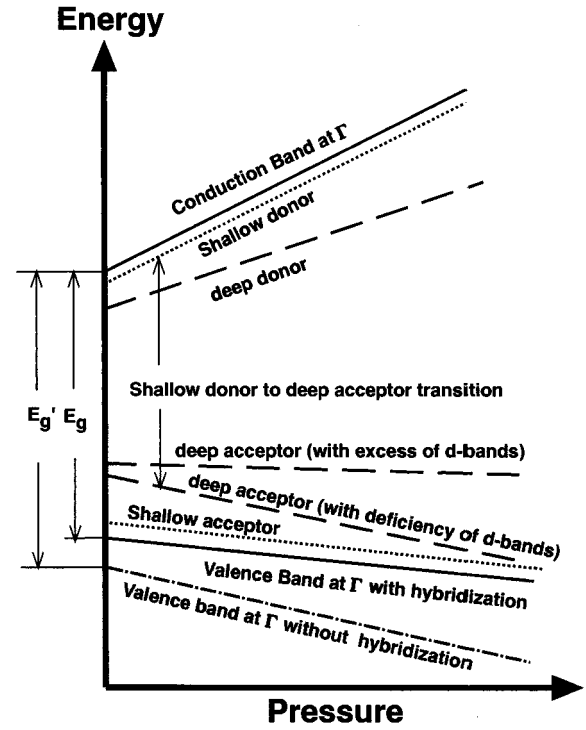


FIG. 8. Schematic diagram of the pressure dependence of the conduction band, the valence band, shallow and deep donors, shallow and deep acceptors in chalcopyrite semiconductors showing the effect of  $p$ - $d$  hybridization on the valence bands and the deep acceptors.  $E_g$  and  $E_g'$  represent, respectively, the band gaps of a chalcopyrite semiconductor and its zinc-blende analog.

TABLE I. Comparison between pressure coefficients of band gaps, excitons, and defect emission peaks in  $\text{AgGaS}_2$ ,  $\text{AgGaSe}_2$ , and  $\text{CuGaS}_2$ . The pressure coefficients were obtained by least-square fits to the data points in Fig. 4 with the standard deviations given as the uncertainties in the fit.

Pressure coefficient (meV/GPa)	$\text{AgGaSe}_2^a$	$\text{AgGaS}_2$	$\text{CuGaS}_2$
Band gap (300 K)	51	44.5	38.8
Band gap (<77 K)			41.6
Exciton (<77 K)	38	40.5 <sup>b</sup> 37.3 <sup>c</sup>	41.7
Shallow center emission peaks		40.5 ± 1.5 (P2) 37 ± 0.8 (A, A')	
Shallow donor to deep acceptor transitions	69(300 K) 46(77 K)	57.6 ± 2 (B, B')	67(B) 24(C)
Deep donor to deep acceptor transitions		54 ± 1(D) 41 ± 2(E)	

<sup>a</sup>From Ref. 16.

<sup>b</sup>From Ref. 15.

<sup>c</sup>From Ref. 17.

ment we have found that doping Cd into AgGaS<sub>2</sub> introduces deep centers whose emission peak has the same pressure coefficient as the peaks *B* and *B'* found in undoped AgGaS<sub>2</sub>. While doping Au into the same material introduces an emission peak whose pressure coefficient is identical to that of the peak *C* observed previously. In unintentionally doped CuGaS<sub>2</sub> we have found both PL peaks with pressure coefficients larger (peak *B*) and smaller (peak *C*) than the band gap. Our explanation of these results is presented below.

In semiconductors with the diamond- and zinc-blende-type crystal structures, it is well known that the pressure dependences of shallow and deep centers are often quite different. A shallow center derives its wave function from the nearest band extremum and hence their pressure dependences are the same. On the other hand, a deep center wave function can be composed of wave functions from several bands over a large region of the Brillouin zone. As a result its pressure dependence is not necessarily the same as those of its nearest band extremum.

The pressure coefficient of the absorption edge  $dE_g/dP$  of a direct-band-gap semiconductor, such as GaAs, is equal to the difference between the pressure coefficients of the conduction-band minimum and the valence-band maximum both at the zone center ( $\Gamma$  point):

$$\frac{dE_g}{dP} = \frac{dE_c}{dP} - \frac{dE_v}{dP}. \quad (2)$$

In zinc-blende-type semiconductors  $dE_c/dP$  is large and positive since the conduction band at  $\Gamma$  is derived mainly from the *s-like antibonding* orbitals while  $dE_v/dP$  is small and negative because the valence band is derived from the *p-like bonding* orbitals. These results are shown schematically in Fig. 8. An optical transition between a shallow donor and a shallow acceptor should have a pressure coefficient  $dE_{\text{DAP}}/dP$  (where  $E_{\text{DAP}}$  is the donor-acceptor pair transition energy) very similar to that of the band gap. However, if the transition involves a deep donor and shallow acceptor then  $dE_{\text{DAP}}/dP$  is expected to be *smaller* than  $dE_g/dP$ . The reason is that the pressure coefficients of the conduction band at critical points such as *L* and *X* in zinc-blende-type semiconductors are either smaller than at  $\Gamma$  or negative in sign.<sup>14</sup> Thus a deep donor whose wave function is a linear combination of the wave functions throughout the entire Brillouin zone will have a coefficient *smaller* than that of the conduction-band minimum at  $\Gamma$  (Ref. 13) as shown in Fig. 8. In fact, to our knowledge, there has been no report of a defect emission peak with pressure coefficients *larger* than that of the band gap at  $\Gamma$  in zinc-blende-type semiconductors. Thus the observation of emission peaks with pressure coefficients larger than that of the band gap in three chalcopyrite semiconductors must be attributed to some fundamental difference between the band structure of these materials and those of the zinc-blende-type semiconductors.

Discussions of the band structure of chalcopyrite semiconductors with the formula I-III-VI<sub>2</sub> usually begin with the observation that their crystal structure can be regarded as being composed of two unit cubes of the zinc-blende (ZnS) crystal stacked on top of each other along the [100] axis. Half of the cations in ZnS are replaced by group I transition-metal ions while the other half are replaced by group-III

ions. Thus for every chalcopyrite semiconductor, one can identify a corresponding II-IV “zinc-blende analog.”<sup>19</sup> For example, the analog of CuGaS<sub>2</sub> is ZnS while that of AgGaS<sub>2</sub> is Cd<sub>0.5</sub>Zn<sub>0.5</sub>S. The band gaps of the chalcopyrite semiconductors are significantly smaller than their II-VI zinc-blende analogs resulting in the so-called “band-gap anomaly” (denoted by a negative  $\Delta E_g$ ). This has been explained by hybridization of the *d* electrons of the transition-metal cations with the *p-like* valence bands.<sup>19</sup> Since the *d* bands of transition-metal ions such as Ag and Cu are lower in energy than the valence-band maximum at  $\Gamma$ , hybridization pushes up the valence-band maximum and hence decreases the band gap (the contribution of this effect to  $\Delta E_g$  will be represented as  $\Delta E_g^d$  with  $\Delta E_g^d < 0$ ) as shown in Fig. 8. Jaffe and Zunger<sup>19</sup> have shown that there are additional contributions to the “band-gap anomaly.” One of these (abbreviated as  $\Delta E_g^S$  where *S* stands for structure) results from the difference between the I-VI and III-VI bond lengths and from the deviation of the *c/a* ratio (where *a* and *c* are lattice constants of the tetragonal unit cell) from 2. Another effect (labeled  $\Delta E_g^{\text{CE}}$  where CE stands for cation electronegativity) arises from the difference in the cation electronegativity between the zinc-blende analog and the corresponding chalcopyrite compound.

Based on the above model for the band structure of the chalcopyrite compounds, we can understand the effect of pressure on the band-gap anomaly. Since  $\Delta E_g^{\text{CE}}$  is insensitive to lattice spacing we shall neglect its contribution to the pressure coefficient. To determine the effect of pressure on  $\Delta E_g^S$  it is necessary to know the pressure dependence of internal structural parameters, such as the difference between the I-V and III-V bond lengths. In general these internal parameters are not determined uniquely by the lattice parameters such as *a* and *c*. In the case of AgGaS<sub>2</sub> it has been shown that the internal structural parameters are independent of pressure.<sup>20</sup> We shall assume that the dominant effect of pressure, in AgGaS<sub>2</sub> at least, is to change  $\Delta E_g^d$ . Reducing the distance between the group I cations and the anions should have the effect of enhancing the *p-d* hybridization and hence increasing the *magnitude* of  $\Delta E_g^d$  or  $d\Delta E_g^d/dP$  is negative. If we express  $dE_g/dP$  of the I-III-VI<sub>2</sub> compound as  $dE_g/dP = dE'_g/dP + d\Delta E_g^d/dP$ , where  $dE'_g/dP$  is the pressure coefficient of its zinc-blende analog then  $dE_g/dP < dE'_g/dP$  since  $d\Delta E_g^d/dP$  is negative. Another effect of hybridization on the band-gap pressure coefficient can be derived by considering the valence-band wave function as a linear combination of *p-like* and *d-like* functions. The *p-like* component has a small negative pressure coefficient while the *d-like* component essentially has no pressure dependence. Increasing pressure has the effect of increasing the *d-like* component in the valence band and hence decreases the pressure dependence of the valence band. In cases where the valence band has a negative pressure dependence in the absence of hybridization, both effects considered tend to reduce the pressure coefficient of the valence band. The pressure dependence of the valence band for different amounts of *p-d* hybridization are shown schematically in Fig. 8.

The case of AgGaS<sub>2</sub> is often cited as a typical example of the reduction in band-gap pressure coefficient resulting from hybridization. Jayaraman *et al.*<sup>21</sup> and Takarabe *et al.*<sup>22</sup> have reported  $dE_g/dP$  to be 22 and 20 meV/GPa, respectively, in

AgGaS<sub>2</sub> while the corresponding coefficient  $dE'_g/dP$  in II-VI selenide semiconductors are about 60–70 meV/GPa.<sup>23</sup> More recent results<sup>15</sup> have, however, shown that  $dE'_g/dP$  of AgGaS<sub>2</sub> is of the order of 40 meV/GPa (see Table I). Thus the reduction in  $dE'_g/dP$  of chalcopyrite semiconductors is about 10–20 meV/GPa and can be explained mostly by the presence of  $p$ - $d$  hybridization in the valence band.

### A. AgGaS<sub>2</sub>

From the above discussions we can understand the pressure coefficients of the emission peaks in AgGaS<sub>2</sub>. The peaks  $A$ ,  $A'$ , and  $P2$  in Fig. 4 all have about the same pressure coefficients as the exciton (EX) and hence they involve shallow levels. The peaks  $B$  and  $B'$ , on the other hand, must be associated with deep centers since their pressure coefficients are much larger than that of the exciton. As we have suggested previously,<sup>15</sup> these peaks involve transitions between *deep acceptors* and shallow donors with activation energies of 16.5 and 26.5 meV, respectively. The reason why a deep acceptor can give rise to a transition with pressure coefficient larger than the band gap in chalcopyrite semiconductors can be explained by the effect of  $p$ - $d$  hybridization in these materials. As pointed out above this hybridization reduces the band-gap pressure coefficient of the chalcopyrites relative to that of their zinc-blende analogs. Suppose a deep acceptor draws its wave function entirely from the  $p$  orbitals and not at all from the  $d$  orbitals, then such a “ $d$ -orbitals deficient” deep acceptor will have a stronger pressure dependence than the valence-band edge (see Fig. 8). In fact its pressure coefficient can be very close to that of the valence-band edge in the “zinc-blende analog.” Thus the pressure coefficient of a transition from a shallow donor to this deep acceptor will be about the same as  $dE'_g/dP$ , the band-gap pressure coefficient in its “zinc-blende analog.” For AgGaS<sub>2</sub> this means that the pressure coefficient of a shallow-donor-to-deep-acceptor transition will be comparable to the  $dE'_g/dP$  of Cd<sub>x</sub>Zn<sub>1-x</sub>S, which is equal to 55 meV/GPa. Indeed we find that the peaks  $B$ ,  $B'$ , and  $D$  all have nearly the same pressure coefficients of around 58 meV/GPa. In the case of AgGaSe<sub>2</sub> the deep level transition reported in Ref. 16 has a pressure coefficient of 46 meV/GPa at 77 K while the exciton pressure coefficient is 38 meV/GPa (see Table I). The band-gap pressure coefficient of its zinc-blende analog Cd<sub>x</sub>Zn<sub>1-x</sub>Se is 60 meV/GPa. Presumably in this case the deep acceptor wave function still contains some contribution from  $d$  electrons and as a result its pressure coefficient is smaller than that of the valence band in the zinc-blende analog.

We noted that the peak  $D$  is introduced by doping the AgGaS<sub>2</sub> sample with Cd. In principle substitutional Cd<sub>Ga</sub> most likely forms shallow acceptors since the core of Cd atoms is not too different from that of Ga atoms. Such shallow acceptors may be responsible for the shallow acceptors involved in peaks  $A$  and  $A'$  whose pressure dependence closely follows that of the band gap. However, they cannot explain the behavior of peak  $D$ . Neither can substitutional Cd<sub>Ag</sub>, which form donors. Thus the deep acceptors introduced by Cd in AgGaS<sub>2</sub> are probably not simple substitu-

tional defects. The fact that the deep acceptor responsible for peak  $D$  has a deficiency in  $d$  orbitals suggests that it may be located on Ag sites such as Ag vacancies. Such intrinsic defects may also explain the similarity between the pressure dependence of the peak  $D$  and the peaks  $B$  and  $B'$  in unintentionally doped samples.

The activation energy of the peak  $E$  in Au-doped AgGaS<sub>2</sub> obtained from Fig. 2 is 54 meV, almost twice the expected binding energy of shallow donors in AgGaS<sub>2</sub>. This activation energy is consistent with deep donor binding energies in AgGaS<sub>2</sub> quoted in the literature.<sup>11</sup> In addition peak  $E$ 's energy is lower than that of peak  $D$  by 0.24 eV. These results strongly suggest that peak  $E$  involves both deep donors and deep acceptors. This is not too surprising since transition-metal impurities such as Au are known to form deep centers in zinc-blende-type semiconductors.<sup>24</sup> In the chalcopyrite materials substitutional defects such as Au<sub>Ga</sub> can be double acceptors while interstitial Au can be deep donors. However, in zinc-blende-type semiconductors the energies of transition-metal deep centers are much less sensitive to pressure than that of the band edges<sup>25</sup> while peak  $E$  has almost the same pressure dependence as the band gap. We suggest that this is probably due to a fortuitous cancellation between the reduction in the pressure coefficients of the deep donor and deep acceptor responsible for peak  $E$ . The existence of the peak  $C$  with a very similar pressure dependence in the unintentionally doped samples can presumably be explained by intrinsic deep centers such as interstitial Ag and Ag anti-site defects such as Ag<sub>Ga</sub>.

### B. CuGaS<sub>2</sub>

The results in the unintentionally doped CuGaS<sub>2</sub> shown in Fig. 7 can be interpreted in the same ways as in the unintentionally doped AgGaS<sub>2</sub>. The peak  $B$  in CuGaS<sub>2</sub> has a pressure coefficient larger than that of the exciton (see Table I) and therefore involves a shallow donor and a deep acceptor. The activation energy of the shallow donor has been determined previously to be 11 meV.<sup>8</sup> The zinc-blende analog of CuGaS<sub>2</sub> is the II-VI compound ZnS with a band gap pressure coefficient of 64 meV/GPa.<sup>23</sup> We note that this pressure coefficient is quite close to that of peak  $B$ , suggesting that  $B$  is associated with a deep acceptor with a “deficiency in  $d$  bands” also. In the case of peak  $C$  in CuGaS<sub>2</sub> we have deduced a donor activation energy of about 10 meV from its temperature dependence.<sup>8</sup> Thus we had to attribute this peak to a transition between a shallow donor and a different deep acceptor. This deep acceptor has a much larger binding energy than the one involved in peak  $B$ . It must also have a very small pressure coefficient in order that the transition between a shallow donor and this deep acceptor has a pressure coefficient much smaller than the band gap. This suggests that, in contrast to those deep acceptors with a deficiency in  $d$  orbitals, this deep center has a greater contribution from  $d$  electrons than even the hybridized valence band. The pressure dependence of such deep centers “with an excess of  $d$  bands” is shown schematically in Fig. 8 for comparison with other kinds of acceptors.

## CONCLUSIONS

In conclusion we have studied the pressure dependence of

defect-induced emission peaks in AgGaS<sub>2</sub> doped with Cd and Au and in unintentionally doped CuGaS<sub>2</sub>. We found in both materials transitions involving deep acceptors with pressure coefficients larger than that of the band gap. We have explained these results as due to *p-d* hybridization in the valence band of the chalcopyrite compounds. In CuGaS<sub>2</sub> we have observed a transition involving a deep acceptor with a pressure dependence *smaller* than that of the band gap.

*Note added in proof.* We are grateful to Dr. J. D. Chadi for pointing out to us that deep acceptors whose binding energies decrease with pressure have been investigated in zinc-blende II-VI semiconductors both theoretically [C. H. Park and D. J. Chadi, *J. Phys. Chem. Solids* **56**, 585 (1995)]

and experimentally [M. Li, D. J. Strachan, T. M. Ritter, M. Tamargo, and B. A. Weinstein, *Phys. Rev. B* **50**, 4385 (1994)].

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- <sup>1</sup>G. D. Boyd, H. Kasper, and J. H. McFee, *IEEE J. Quantum Electron.* **7**, 563 (1971).
- <sup>2</sup>S. Wagner, J. L. Shay, P. Migliorator, and H. M. Kasper, *Appl. Phys. Lett.* **25**, 434 (1974).
- <sup>3</sup>A. M. Gaber, J. R. Tuttle, D. S. Albin, A. L. Tennant, and M. A. Contreras, in *12th NREL Photovoltaic Program Review*, edited by Rommel Noufi, AIP Conf. Proc. No. 306 (American Institute of Physics, New York, 1994), p. 59.
- <sup>4</sup>Y. X. Fan, R. C. Eckardt, R. L. Byer, R. K. Route, and R. S. Feigelson, *Appl. Phys. Lett.* **45**, 313 (1984).
- <sup>5</sup>D. S. Bethune and A. C. Luntz, *Appl. Phys. B* **40**, 107 (1986).
- <sup>6</sup>S. Shirakata, K. Murakami, and S. Isomura, *Jpn. J. Appl. Phys.* **28**, 1728 (1989).
- <sup>7</sup>J. Hedstrom, H. Ohlsen, M. Bodegard, A. Kylner, L. Stolt, D. Hariskos, M. Ruckh, and H. W. Schock, in *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1993), p. 364.
- <sup>8</sup>I. H. Choi and P. Y. Yu, *J. Phys. Chem. Solids* **57**, 1695 (1996).
- <sup>9</sup>P. W. Yu, W. J. Anderson, and Y. S. Park, *Solid State Commun.* **13**, 1883 (1973).
- <sup>10</sup>P. W. Yu and Y. S. Park, *J. Appl. Phys.* **45**, 823 (1974).
- <sup>11</sup>J. P. Aicardi, J. P. Leyris, and A. Poure, *J. Appl. Phys.* **53**, 1690 (1982).
- <sup>12</sup>G. Massé, *J. Appl. Phys.* **58**, 930 (1985).
- <sup>13</sup>For experimental work, see for example, D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, in *Proceedings of the 17th International Conference on the Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer-Verlag, Berlin, 1985), pp. 627–630.
- <sup>14</sup>For theoretical discussions, see, for example, D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **61**, 873 (1988); *Phys. Rev. B* **39**, 10 063 (1989).
- <sup>15</sup>I. H. Choi and P. Y. Yu, *Phys. Status Solidi B* **198**, 251 (1996).
- <sup>16</sup>I. H. Choi and P. Y. Yu, *Appl. Phys. Lett.* **64**, 1717 (1994).
- <sup>17</sup>K. Reimann, St. Rübenaacke, and M. Steube, *Solid State Commun.* **96**, 279 (1995).
- <sup>18</sup>S. Shirakata, K. Murakami, and S. Isomura, *J. Appl. Phys.* **68**, 291 (1990).
- <sup>19</sup>J. E. Jaffe and A. Zunger, *Phys. Rev. B* **29**, 1882 (1984).
- <sup>20</sup>Y. Mori, K. Takarabe, S. Iwamoto, S. Minomura, E. Niwa, and K. Masumoto, *Phys. Status Solidi* **198**, 427 (1996).
- <sup>21</sup>A. Jayaraman, V. Narayanamurti, H. M. Kasper, M. A. Chin, and R. G. Maines, *Phys. Rev. B* **14**, 3516 (1976).
- <sup>22</sup>K. Takarabe, S. Hitomi, Y. Mori, S. Minomura, E. Niwa, and K. Masumoto, in *High Pressure Science and Technology*, AIP Conf. Proc. No. 309 (American Institute of Physics, New York, 1994), p. 601.
- <sup>23</sup>A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, *J. Phys. Chem. Solids* **11**, 140 (1959); R. L. Knell and D. W. Langer, *Phys. Lett.* **21**, 370 (1966); D. A. Gulino, L. R. Faulkner, and H. G. Drickamer, *J. Appl. Phys.* **54**, 2483 (1983); K. Reimann, *High Pressure Res.* **15**, 73 (1996).
- <sup>24</sup>For energies of Au deep centers in group IV and III-V semiconductors see Vol. 22, *Semiconductors. Intrinsic Properties of Group IV Elements, and III-VI, II-VI and I-VII Compounds*, Landolt-Börnstein New Series, Group III, Vol. 22, Pt. a (Springer-Verlag, Berlin, 1987).
- <sup>25</sup>D. D. Nolte, W. Walukiewicz, and E. E. Haller, *Phys. Rev. Lett.* **59**, 501 (1987).