Origin of the deep center photoluminescence in $CuGaSe_2$ and $CuInS_2$ crystals

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Photoluminescence (PL) of $CuGaSe_2$ and $CuInS_2$ single crystals, either as grown or Cu annealed, reveals a broad and clear deep emission band at $h\nu \approx E_g - 0.6$ eV. In both of these as-grown materials this band has a similar doublet structure with the two $D1$,$D2$ subbands separated by about 100 meV. After the Cu annealing all samples became highly compensated and an additional deep PL band (W band) appeared on the high energy side of these D bands. This suggests a closely similar origin of the emission for the both materials. By a straightforward model calculation we show that the changes in the shape and intensity of these emission bands—due to variation of temperature, excitation intensity or due to the Cu annealing—are well explained if we assume that the $D1$ and $D2$ PL subbands originate in the recombination between the closest and the second closest donor–acceptor pairs, with the essential ingredient of the emission center being an interstitial donor defect, i.e., either Cu_i or Ga_i in $CuGaSe_2$ and Cu_i or In_i in $CuInS_2$. The W band in both compounds appears to be due to the recombination of an electron from this deep donor level with a hole in a deep localized state of the valence band tail.
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I. INTRODUCTION

The ternary chalcopyrite semiconductors I–III–VI_2 have attracted considerable interest as candidates for applications in the areas of light emitting diodes and photovoltaic devices. In spite of significant experimental and theoretical efforts devoted to the fundamental studies of the properties of these materials, and to the successful preparation of quite efficient devices based on them, the overall understanding is not yet as clear as we would like it to be. This is, partly at least, due to the fact that the complex defect structures of these compounds are not well understood.

Photoluminescence (PL) spectroscopy is a very general and widely used method to analyze the defect structure of semiconductors. Unfortunately, most of the PL studies of chalcopyrite semiconductors, so far, have been focused on relatively shallow PL bands having a peak position near the band gap energy. Much less is known about possible deep PL bands, with emission energies $h\nu < E_g - 0.4$ eV and, as a result of this, about the related deep electronic gap levels in these compounds. We have good reason to believe that these deep levels do play an important role in the optoelectronic properties.

$CuGaSe_2$ and $CuInS_2$ have relatively large band gaps of $E_g = 1.68$ and 1.53 eV, respectively, and therefore they are the most suitable materials for deep level PL studies. Deep PL bands in $CuGaSe_2$ have been reported at 1.18 and 1.02 eV[1,2] and at 1.142 eV.[3] In $CuInS_2$, also, several deep PL bands have been at least mentioned.[4,5].

There exists no firmly established model of these deep PL bands so far. This paper presents the first systematic study and comparison of the deep PL bands in $CuGaSe_2$ and $CuInS_2$.

II. EXPERIMENT

$CuGaSe_2$ and $CuInS_2$ single crystals were grown in closed ampoules from a stoichiometric mixture of the elements ($6N$ purity) by chemical vapor transport at temperatures between 800 and 750 °C using iodine (about 3 mg/cm^3) as the transport agent. Some of the crystals were also grown by the vertical Bridgman technique. The p-type single crys-

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tals had typical dimensions of $0.5\times4\times6$ mm^3 with well pronounced (112) surfaces, which is characteristic of ternary Cu chalcopyrites. The Cu annealing experiments were carried out in a closed system horizontal furnace at temperatures ranging from 400 to 700 °C for annealing times of up to 120 h in an inert gas flow. A small piece of Cu was mounted about 3–4 cm upstream of the sample. The final sample composition was analyzed by x-ray fluorescence measurements, which revealed no significant amounts of extrinsic impurities introduced during the growth process or due to the different annealing treatments.

Resistivity and Hall-effect measurements were carried out in the temperature range from 30 to 400 K using a conventional dc measurement setup equipped with a closed-cycle He cryostat. Ohmic contacts were prepared by evaporating Au dots on *p*-type samples.

A Kr ion laser (Spectra Physics model 165) at a wavelength of 568.2 nm was used as the excitation source for steady-state PL measurements at temperatures ranging from 2 to 300 K. The laser beam was focused onto the sample with a spot diameter of about 100 μm and the luminescent light was analyzed with a GCA/McPherson Instruments 1 m grating monochromator (Czerny–Turner type) and detected by either a liquid nitrogen cooled germanium detector (North Coast EO-817L) or a photomultiplier tube with $S1$ characteristics. All samples were etched prior to measurement in a solution of bromine in methanol in order to ensure good and comparable surface properties.

III. RESULTS AND DISCUSSION

Two types of samples were used in this study: (1) as-grown and (2) compensated. Most of the as-grown $CuGaSe_2$ and $CuInS_2$ crystals had quite low resistivity values. After the Cu annealing all crystals became highly compensated and the resistivity increased by more than 3 orders of magnitude. These two types of crystals also had very different PL spectra both in the edge emission region and in the ''deep'' region. The edge emission of compensated samples was dominated by an asymmetric broad PL band while in the as-grown samples several narrow PL bands were present. It is known that in the highly compensated samples conduction and valence band edges are often disturbed by the potential fluctuations of charged defects and, therefore, so-called band tails are formed.[6,7] Due to the relatively large effective hole mass of ternary compounds, localized hole states are easily formed within the valence band tails, which affect the shape of the edge emission bands, especially in compensated samples.

Low temperature PL spectra from the ''deep'' region of the two compounds studied are shown in Fig. 1. In both of the as-grown crystals the PL spectra consist of two distinct PL bands $D1$ and $D2$, while in the compensated crystals a new W band appears on the high energy side of the spectra. The parameters of these PL bands obtained from the Gaussian fitting of the spectra are presented in Table I. Annealing of as-grown $CuGaSe_2$ crystals in vacuum or in a Ga atmosphere reduces the intensity of these deep PL bands. The same behavior was detected also in $CuInS_2$. At the same time, the Cu annealing always increased the intensity of the deep PL bands in both compounds.

Several observations can be made from the measured PL spectra:

(a) The half width of the $D2$ band always exceeds the half width of the $D1$ band;
(b) the peak positions of both $D1$ and $D2$ bands do not differ much between as-grown and compensated samples, but the half width of both bands increases in the compensated samples;
(c) the half width of the W band is larger than that of other bands; and
(d) the energetic distance between $D1$ and $D2$ bands is about 105 and 90 meV in $CuGaSe_2$ and $CuInS_2$, respectively, i.e., it is about 15 meV smaller in $CuInS_2$.

From the temperature dependence of the PL spectra, shown for the $CuGaSe_2$ compensated sample in Fig. 2, one observes that the W band quenches very rapidly as T increases. Therefore, it was not possible to determine the precise magnitude of the thermal quenching activation energy for this band, but the activation energies for $D1$ and $D2$ bands are given in Table II. It is worth noticing that the activation energy for the $D1$ band is always smaller than for the $D2$ band, and that the peak positions of the two D bands either remain unchanged or change very little with temperature. Therefore we must exclude the possibility that the conduction or valence band states are involved in the recombination process of the D bands.

It is also of interest that the peak positions of the D bands did not seem to shift with increasing excitation power (see Fig. 3). From this we conclude that we also must rule out the model of distant donor–acceptor pairs (DAPs), where a shift toward higher energies is expected.[8] Further, we observe from Fig. 3 that the intensity of the $D2$ band shows a steeper dependence upon excitation power than that of the $D1$ band. The dependence of the integrated intensity Φ of the D bands on the excitation laser power I can be represented as $\Phi\sim I^{\alpha}$. For $D1$ and $D2$ bands the parameter α has values of 0.73 and 1.03, respectively. This rather big difference indicates that these two bands must have somehow different origins.

The overall properties of the deep PL bands in $CuGaSe_2$ and $CuInS_2$ are very similar to each other and therefore it is reasonable to believe that they have a related origin in both compounds. Even more, they actually seem to have properties comparable to those of the deep bands in CdTe.[9,10] The pertinent deep donor–deep acceptor defect model was proposed for the deep PL bands in CdTe.[9] According to this model the deep PL bands arise from a DA recombination between pairs of the nearest neighbors ($D1$ band), and between pairs of the next-nearest neighbors ($D2$ band), respectively, so that the DAP pairs are chemically identical but structurally slightly different. It is known that the emission energy from a DA pair separated by a distance r is obtained from[8]

$$E(r)=E_g-(E_A^0+E_D^0)+\frac{Z_D Z_A e^2}{\epsilon r}-\Gamma(r). \tag{1}$$

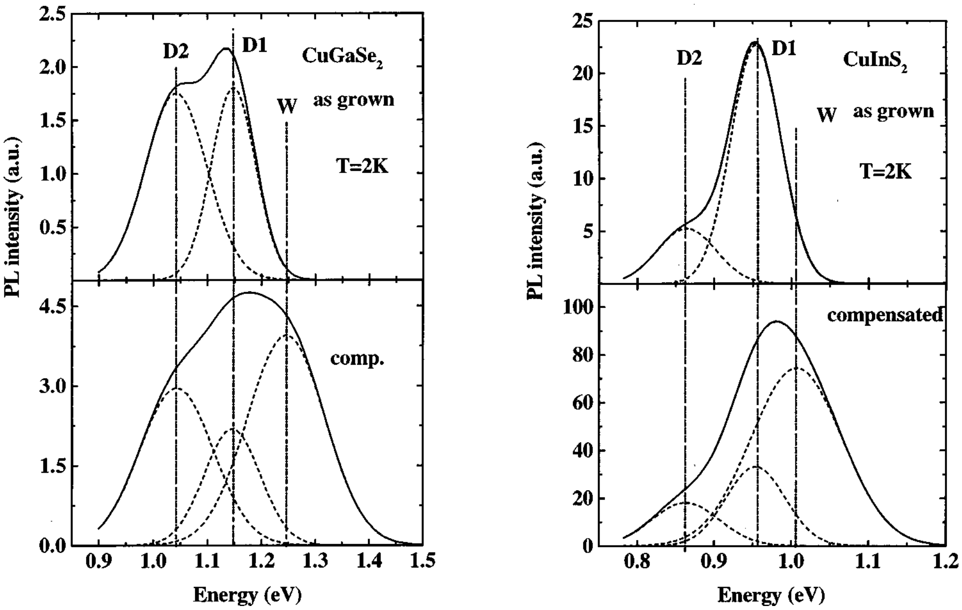

FIG. 1. Photoluminescence spectra over the ''deep'' spectral region of $CuGaSe_2$ and $CuInS_2$ as-grown and compensated crystals. Individual Gaussian subbands obtained from the spectral fitting are shown as dashed curves.

Here E_g is the band gap energy, E_A^0 and E_D^0 the acceptor and donor ionization energies, ϵ is the dielectric constant Z_D, Z_A are the charges of donor and acceptor, respectively, and $\Gamma(r)$ is an additional term which includes interactions relevant at very short distances only. There are different opinions regarding the details of this last term (see for example Ref. 8), but the main result is that it gives only minor, second order corrections to Eq. (1). However, as it was shown by Williams,[8] the magnitude of $\Gamma(r)$ may exceed 25 meV or even more in case of very short DA distances. Therefore, the theoretically calculated Coulombic energy is usually higher than the energy found from experiment. An open question is the appropriate value for the dielectric constant ϵ in the case of very close pairs. In compound semiconductors it is obvious that ϵ must be a combination of both optical and static dielectric constants, but the exact numerical value for it is hard to predict. Therefore, Eq. (1) must be considered as a very rough method to calculate the transition energy of close DA pairs.

It is also known that the electron (hole) wave function in the deep donor (acceptor) level must be highly localized. Because of this, for more distant pairs, there is practically no overlap of the initial and final state wave functions and, as a result of this, no observable recombination emission. It seems to be a reasonable assumption that both the donors and the acceptors can occupy only certain energetically favorable positions within the chalcopyrite crystal. Then it is possible to calculate, using Eq. (1), the approximate energy separations ΔE between the DA pairs of the nearest or the next-nearest neighbors, respectively,

$$\Delta E = \frac{Z_D Z_A e^2}{\epsilon}\left(\frac{1}{r_1} - \frac{1}{r_2}\right). \qquad (2)$$

In Eq. (2) r_1 is the shortest DA distance and r_2 the next shortest one. Although the components of a DAP pair could, in principle, be positioned at a lattice site or at an interstitial position, our calculation, based on Eq. (2), indicates that one of the DAP components is at an interstitial position and the other one is at a lattice site, next to it.

It is known that in both of the compounds studied here the crystal lattice is affected by the tetragonal distortion and therefore the group-VI anions (Se and S) are slightly displaced from their ideal positions. In addition, it is known that atomic positions around a defect are relaxed. We may assume that the highest value of displacement of nearby ions is obtained in the case of vacancies. As it was shown[11] in Sobolev *et al.*, in the ternaries it is expected that the lattice relaxation near vacancies gives less than a 10% displacement for the bond lengths of nearby ions. Thus it is safe to assume that the lattice relaxation, as such, never contributes an error exceeding about 10% in our ΔE calculations. All these facts make it difficult to claim precise and correct calculated values of ΔE, but, nevertheless, we can obtain a first order approximation.

We use the lattice parameters $a = 0.5607$ nm, $c = 1.1054$ nm for $CuGaSe_2$,[12] and $a = 0.5523$ nm, $c = 1.1123$ nm for $CuInS_2$.[13] Values $\epsilon = 10.2$ for $CuInS_2$,[14] and $\epsilon = 9.6$ for $CuGaSe_2$,[15,16] and $Z_A = 1$ were used in calculations. Note that there are also just two types of interstitial positions in the chalcopyrite lattice (i_1 and i_2). Taking the unit cell corners to be defined by the cations (i.e., at each corner either Cu or Ga), these interstitial positions have the coordinates (1/2; 1/2; 1/4) and (3/4; 3/4; 3/8), respectively. It is important to realize that these two interstitials have a different surrounding. The first one (i_1) is surrounded by six cation sites and four anion sites, and the second one (i_2) by four cation sites and six anion sites, respectively. The results of the numerical calculations, for two possible charge states of the donor, are given in Table III. In the present calculation the interstitial ions were taken to be point charges positioned symmetrically within the interstitial volume.

From Table III it becomes clear that donor and acceptor pairs cannot be situated in positions such as $D_{Cu}-A_{Se}$,

TABLE I. Average experimental values of the deep PL bands peak positions $h\nu_{max}$ and half widths $W_{1/2}$ in $CuGaSe_2$ and $CuInS_2$ as-grown and compensated crystals.

	W band		*D*1 band		*D*2 band	
$CuGaSe_2$	as-grown	compens.	as-grown	compens.	as-grown	compens.
$h\nu_{max}$ (eV)	—	1.246	1.148	1.146	1.042	1.043
$W_{1/2}$ (meV)	—	169.5	96.5	122.5	134.2	160.1
$CuInS_2$						
$h\nu_{max}$ (eV)	—	1.007	0.954	0.954	0.864	0.863
$W_{1/2}$ (meV)	—	138.9	76.5	90.7	89.4	103.6

A_{Cu}–D_{Se}, D_{Ga}–A_{Se}, A_{Ga}–D_{Se}, D_{In}–A_S, A_{In}–D_S, D_{Cu}–A_{In} or A_{Cu}–D_{In}, because the calculated ΔE value is not consistent with the experimentally observed energy separation between the $D1$ and $D2$ PL bands, i.e., 105 and 90 meV for $CuGaSe_2$ and $CuInS_2$, respectively. The possibility that the DAP is situated at lattice sites such as A_{Cu}–D_{Ga}, D_{Cu}–A_{Ga} or A_{Cu}–D_{In}, D_{Cu}–A_{In} is, however, also quite improbable due to the rather small calculated value of the energy separation ΔE in the case of $Z_D=1$. In this case, also, both the donor and the acceptor would have the same surrounding in the first and second coordination spheres and—it is apparent—the half width, in the first approximation at least, of the corresponding PL bands should also be the same. However, the experimentally observed difference in the half widths can clearly be explained in the case where one component of the DAP is located at an interstitial position. These different surroungings of the two possible interstitial positions i_1 and i_2 would seem to explain in quite a natural way the experimentally observed different half widths of the PL bands—both qualitatively and quantitatively.

As it can be seen from Table III, the calculated values of ΔE are somewhat smaller than the experimental ones for both compounds in the case of $Z_D=1$, but considering the roughness of our calculations the obtained result is reasonable. In the case of $Z_D=2$ the situation is opposite and, considering the possible effect of the additional term $\Gamma(r)$ in Eq. (1), may give an even more realistic result. Furthermore, in line with the present experimental observation, the calculated ΔE turned out to be smaller for $CuInS_2$ than for $CuGaSe_2$. Therefore, we feel that we are able to assert that the $D1$ and $D2$ PL bands are due to a recombination between such DAP states where one of the components is located in either of these two interstitial positions, and the other component is at a lattice site next to it. Considering our annealing experiments it is most probable that we are dealing with a Cu_i—a deep donor defect.

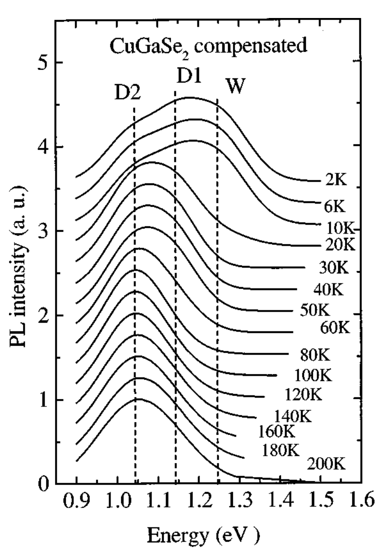

FIG. 2. Normalized PL spectra of compensated $CuGaSe_2$ measured at different temperatures.

It is known that an interstitial copper ion is highly mobile in most ternaries. Therefore all kinds of annealing (except the Cu annealing) should tend to reduce the concentration of Cu_i (and the intensity of the deep PL bands, also) through the simple reaction $V_{Cu}+Cu_i \Rightarrow Cu_{Cu}$. However, the deep donor levels with $E_D>0.4$ eV are not so often observed in $CuInSe_2$ and related ternaries. In Ref. 17 a deep donor level $E_D=0.57$ eV was nevertheless detected in $CuInSe_2$. At the same time the most recent theoretical calculations[18,19] have shown that Cu_i is not such a deep donor in the ternaries and, in fact, apparently does not exceed the value $E_D=0.21$ eV in $CuGaSe_2$. According to the theoretical estimates[18] the deepest donor level in $CuGaSe_2$ is Ga_{Cu} with $E_D=0.49$ eV only. This means that it is difficult to find an intrinsic donor defect with single charge state which would be deep enough to satisfy our model. Therefore we may look at other possibilities. One of them is a donor defect Ga_i having in $CuGaSe_2$ three different charge states Ga_i^{+}, Ga_i^{2+} and Ga_i^{3+}. The same situation applies for the In_i defect in $CuInS_2$. It may be possible that after Cu annealing, the Cu atom substitutes Ga, forming an acceptor Cu_{Ga} and forcing the Ga atom into the interstitial position. Ga_i^{2+} must have a rather deep donor level and it easily forms a DA pair with Cu_{Ga}:$(Cu_{Ga}Ga_i)^{+}$. This DA pair should also give a rather deep donor level which compensates shallow acceptors in $CuGaSe_2$.

It is possible to argue that the simple defects Ga_i, Ga_{Ga}, etc. cannot have large concentrations in the samples, since

TABLE II. Experimentally determined temperature quenching activation energies E_T (meV) for the $D1$ and $D2$ bands in $CuGaSe_2$ (see Fig. 2).

Sample	*D*1 band	*D*2 band
as-grown	55.1	73.0
compensated	59.0	78.4

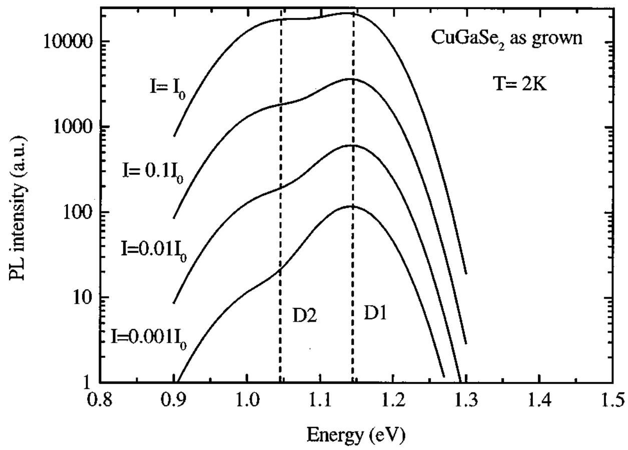

FIG. 3. PL spectra of the as-grown $CuGaSe_2$ as a function of excitation intensity.

they have high formation energies. The latest calculations however have shown[19] that the formation energy of a defect pair is remarkably lower than the sum of two individual defects. Therefore, the concentration of defect pairs may increase considerably, as compared with the concentration of individual defects, if estimated separately.

Another, quite different but maybe rather hypothetical possibility is that copper may be incorporated as an interstitial ion as Cu^{2+}, i.e., having the valence 2. In II–VI compounds Cu^{2+} is usually responsible for infrared (IR) emission. Unfortunately, up to now, there is no experimental evidence of the Cu^{2+} state in copper containing ternaries. Admittedly, there is also a possibility that the deep donor state discussed here is formed by an uncontrolled impurity. We think that this possibility is not a serious one, because we found the same deep PL bands in samples with very different growth conditions and starting materials. It may be that these same interstitial cations play a major role in the recent electronic metastability and ionic electromigration observations in the chalcopyritic materials, done by deep level transient spectroscopy (DLTS),[20] transient ion drift (TID)[21] or radioactive tracer techniques.[22]

It is important to realize that, from a single PL spectrum, there is no trivial way to determine whether the deep DAP PL emission observed comes from a recombination center involving a deep donor or from a pair with a deep acceptor. Our conclusions are based on the overall thermal behavior of the measured PL spectra. If the deep component were an acceptor the temperature quenching usually proceeds in two distinct stages. At the first stage electrons are thermally released from the donor level into the conduction band. After this the c band acceptor recombination follows, giving a PL peak at higher energies and of characteristic shape. This recombination is subsequently quenched at the second stage. In the case of a deep donor defect, the temperature quenching usually shows only one stage, because the deep donor-to-v band recombination has a fairly small probability. In our samples we observed only one stage of thermal quenching and no PL bands appear at the higher energies. This is the main reason leading to our conclusion that we have a deep donor defect.

TABLE III. Calculated approximate energy separation ΔE for various interstitial and lattice site positions. In the table ''Cu–Ga'' actually means donor at the Cu site and acceptor at the Ga site of the chalcopyritic lattice, or vice versa.

	ΔE (meV) ($Z_D=1$)		ΔE (meV) ($Z_D=2$)	
DAP lattice positions	$CuGaSe_2$	$CuInS_2$	$CuGaSe_2$	$CuIns_2$
Cu–Ga, Cu–In	110	106	220	212
Cu–Se, Ga–Se, In–S, Cu–In	298	281	596	562
Cu-i, Ga-i, In-i (i_2,i_1)	86	78	172	156
Se-i, S-i (i_1,i_2)	86	78	172	156

In the PL spectra of all the compensated samples the W band appears at the higher energy side of the $D1$ band (see Fig. 1). It is known that the spatially fluctuating potential of charged defects in compensated materials creates localized states for holes deep in the forbidden gap and at low temperatures the recombination probability through these states is quite high.[6,7] Therefore we assume that the W band emission in both compounds is due to a recombination of an electron from the donor level with a hole in these deep localized states. The corresponding recombination model is illustrated in Fig. 4.

Regarding the precise assignment of the electronic levels (shown schematically in Fig. 4) some uncertainties remain. For instance, we might suspect that the PL emission contains a contribution from a deep acceptor level, such as V_{Cu} in $CuInS_2$, since these defects should be present in the samples. Nevertheless; regarding the DAP pairs given in Table III within our simple ΔE model calculation, we believe that we did not exclude any suitable acceptor defect from being a pair for our deep donor. Thus, although in principle V_{Cu} could be a possible acceptor candidate, we are not able to propose a suitable precisely defined defect pair configuration. Our conclusion remains, at this stage, that there must be a deep interstitial donor defect involved.

IV. CONCLUSIONS

A systematic study of the deep PL bands in $CuGaSe_2$ and $CuInS_2$ was carried out. In both of these materials we found a very similar double deep emission band, but there was a difference between the PL spectra of compensated and as-grown, native p-type samples, respectively. In the as-grown p-type samples only two distinct deep PL bands ($D1$ and $D2$) were present in both compounds. After the Cu annealing all samples became highly compensated and an additional deep PL band (W band) appeared on the high energy side of these D bands. The temperature and the excitation power dependence determination of the photoluminescence intensity, carried out for both compounds, provided very specific and clear information about the nature of the D and the W bands.

It was found that the experimental results for $D1$ and $D2$ PL emissions are consistently explained by a model of donor–acceptor pair luminescence, where both donor and acceptor levels are relatively deep. In this model the $D1$ and $D2$ bands are formed as a DAP recombination between pairs of the closest neighbors, and between pairs of the next-

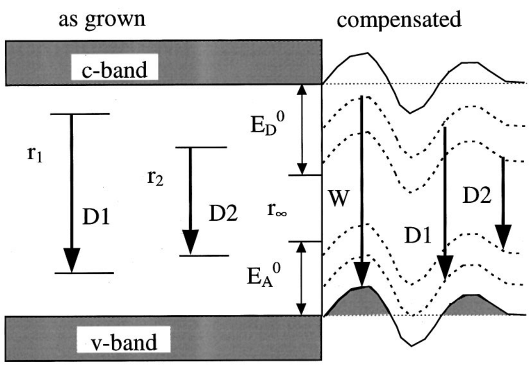

FIG. 4. The recombination model for deep PL bands in $CuGaSe_2$ and $CuInS_2$.

closest neighbors, respectively. We conclude that the DAP defects constituting the $D1$ and $D2$ band recombination centers appear to be chemically identical but structurally slightly different, and that this difference gives rise to the observed difference in the energetic position and the width of the bands. It is further concluded that the donor in these pairs must be an interstitial doubly charged ion, and located in either of the two possible interstitial positions. We also find that the W band emission, which is present both in highly compensated $CuGaSe_2$ and in highly compensated $CuInS_2$, appears to result from the recombination of an electron from this deep donor level with a hole in a deep localized state of the valence band tail.

It was recently shown that a similar interpretation, as given here, was fully compatible with the experimental observations of the deep PL bands in CdTe also.[9,10] Since the I–III–VI_2 chalcopyrites, such as $CuGaSe_2$ and $CuInS_2$, are the simplest ternary analogs of the II–VI zincblende binary compounds, such as CdTe, this appears to provide additional support in favor of our interpretation of the origin of the present deep $D1$ and $D2$ bands.

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