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Reabsorption of the excitonic luminescence in direct band gap semiconductors

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We investigate here the influence of reabsorption on the excitonic luminescence spectrum of $AgGaSe_2$, $CuGaS_2$, and ZnSe under excitation by an electron beam and a He-Cd laser (in the case of ZnSe only). We develop a simple and new theoretical model to analyze our experimental data; it shows that reabsorption should be taken into account in most of our luminescence experiments at 77 K. We believe that such a study provides an interesting method to determine free-exciton energies when they correspond to large absorption coefficients. We have also studied the excitonic luminescence of ZnSe at liquid-helium temperature but, in this case, there is no reabsorption and we think that this is due to strong polariton effects.

I. INTRODUCTION

In direct-band-gap semiconductors, the free exciton is characterized by a large oscillator strength and a large absorption coefficient (10^4–10^6 cm^{-1}). Absorption and reflectivity spectra are well interpreted by the classical exciton theory[1] or, more recently, at low temperature and in pure samples by the polariton theory.[2] However the free-exciton luminescence spectrum is not always as well understood.[3] One of the main problems is that the recombination radiation of free excitons in the bulk is partly reabsorbed before reaching the surface.[3-10]

We wish to describe a detailed and new study of the influence of reabsorption on the excitonic luminescence in some direct-band-gap semiconductors. This study is based on reflectivity, absorption, and radiative-recombination experiments performed in $AgGaSe_2$, $CuGaS_2$ and ZnSe. We report here data obtained at 77 K for all these semiconductors, and we present also similar measurements done in ZnSe at liquid-helium temperature, essentially because we are more interested in this material which might lead to interesting applications. In our luminescence experiments the excitation source was either a He-Cd laser or an electron beam whose energy could be changed between 10 and 35 kV. The depth of the excited layer could thus be varied between a fraction of a micron and a few microns, the idea being that reabsorption should depend on this depth. In $AgGaSe_2$ and $CuGaS_2$ we have also investigated the polarization of the excitonic luminescence with respect to the optical axis because the absorption coefficient (and thus reabsorption) is not the same for both polarizations. To analyze our data we use a simple theoretical model which shows that reabsorption is involved in most of our luminescence experiments at 77 K and gives us a general and interesting method to obtain free-exciton energies when the corresponding absorption coefficients are large. From a similar study we deduce that there is no reabsorption in ZnSe at liquid-helium temperature and we conclude that in this case our data involve important polariton effects. As far as we know, this is the first evidence for such effects in this material.

II. EXPERIMENTAL TECHNIQUES

For the cathodoluminescence measurements, the samples were excited by a pulsed electron beam.[10] The pulse rise time, length, and repetition frequency were, respectively, 5 nsec, 100 nsec, and 200 cps. The electron energy could be varied between 7 and 35 kV; the maximum intensity of the electron beam was 0.1 A/cm^2. In the photoluminescence experiments, the excitation source was a 20-mW cw He-Cd laser working at 3250 Å. The beam was mechanically chopped and focused on a spot of 0.5 mm diameter. The luminescence was collected from the excited face of the sample. The emitted radiation was dispersed by a double pass Perkin-Elmer 99G monochromator and detected by a RTC XP 1020 photomultiplier. The reflectivity and absorption measurements were performed with a HRS 2 Jobin-Yvon monochromator and a Hamamatsu S20 photomultiplier. For the observation of cathodoluminescence, reflectivity, and absorption spectra, the samples were glued with silver paint on the cold finger of an optical cryostat. In the case of the photoluminescence experiments, the sample was immersed in liquid helium or nitrogen.

The samples, which were not intentionally doped, have been prepared by different techniques: ZnSe was obtained by a method[11] derived from the Meis and Fuscher's one,[12] $CuGaS_2$ by transport in gaseous iodine,[13] and $AgGaSe_2$ by the Bridgman method.[14] The crystals used in our experiments were etched in a brome-ethanol solution (ZnSe) or in a mixture of sulphuric acid and potassium bichromate ($AgGaSe_2$ and $CuGaS_2$). The samples were platelets of typical diameter 3 or 4 mm, and their thickness was generally of the order of 0.5 mm for the luminescence measurements.

III. THEORETICAL MODEL

In this section, we want to present a method to analyze the free-exciton luminescence in direct-band-gap semiconductors when reabsorption of the emitted light is not negligible. In the absence of reabsorption, the detailed balance principle shows that the intensity $I(h\nu)$ of the radiation emitted by the sample is connected to the absorption coefficient $\alpha(h\nu)$ as follows[3]:

$$I(h\nu)=\beta(h\nu)^2\alpha(h\nu)[1-R(h\nu)]e^{-h\nu/kT}e^{\mu/kT}, \quad (1)$$

where $R(h\nu)$ is the reflectivity coefficient, μ is the chemical potential of the excitons which are supposed to be thermalized, and β is a constant coefficient. The samples thickness being much larger than the excitation depth d, the intensity of the observed radiation taking into account the reabsorption is

$$I(h\nu)=\beta'(h\nu)^2[1-R(h\nu)]\,\alpha(h\nu)\times e^{-h\nu/kT}\int_0^\infty n(x)e^{-\alpha x}\,dx\,, \quad (2)$$

where x is the depth in the sample from the surface and $n(x)\propto e^{\mu(x)/kT}$ is the exciton density profile. The integral $\int_0^\infty n(x)e^{-\alpha x}dx$ is the Laplace transform $H(\alpha)$ of $n(x)$.

Let us now define the following quantity:

$$\begin{aligned}A(h\nu)&=I(h\nu)/(h\nu)^2[1-R(h\nu)]H(0)e^{-h\nu/kT}\\&=\alpha H(\alpha)/H(0)\\&=A(\alpha)\,.\end{aligned} \quad (3)$$

The first equality in Eq. (3) shows that all the quantities except $H(0)$ in the expression of $A(h\nu)$ can be obtained from reflectivity and luminescence experiments. From the second equality, we see that for a given experiment [$n(x)$ fixed], A is a function of the photon energy $h\nu$ through the absorption coefficient α. For small absorption coefficients ($\alpha d \ll 1$), $H(\alpha)=H(0)$ and A is equal to α. Thus we can obtain $H(0)$ from measurements of the absorption coefficient in the region of the spectrum where it is small (for example, $<10^3$ cm^{-1}) and easy to determine from transmission experiments. Therefore luminescence, reflectivity and absorption experiments will allow us to get $A(h\nu)$.

We wish now to study the general behavior of $A(\alpha)$ to determine typical shapes of $A(h\nu)$, particularly in the case of strong excitonic absorption. For large absorption coefficients ($\alpha d \geq 1$), $A(\alpha)$ depends on the function $H(\alpha)$, i.e., on the exciton profile $n(x)$. Whether the sample is excited by electronic bombardment or by a laser beam, the excitation gives rise to the following phenomena: (i) creation of excitons with a profile $g(x)$; (ii) diffusion and recombination of these excitons. (We do not consider here the formation of excitons from the injected electron-hole pairs because this process is very fast.) The exciton concentration $n(x)$ is governed by the steady-state equation[15]

$$D\frac{\partial^2 n(x)}{\partial x^2}-r+g(x)=0\,, \quad (4)$$

where D is the diffusion coefficient and r the recombination rate of excitons. If S is the surface recombination velocity, the condition at the surface of the sample is

$$\frac{\partial}{\partial x}\,n(0)=\frac{S}{D}\,n(0)\,. \quad (5)$$

The thickness of the sample being much larger than the excitation depth, the exciton concentration must verify another condition:

$$n(\infty)=0\,. \quad (6)$$

The resolution of these equations is generally complicated and depends on the function $g(x)$. However, the condition at the sample surface [Eq. (5)] yields[16] the following result provided that $g(x)$ is not infinite at the surface: when the absorption coefficient increases from 0 to infinity, $A(\alpha)$ increases at first as α, reaches a maximum $A_{\max}$, and then decreases towards an asymptotic value A_∞. Equations (4)-(6) simplify if we assume that the excitons lifetime is independent of the concentration and that their generation is proportional to the intensity of the exciting beam. These conditions are generally satisfied when the excitation is weak, i.e., when there is no exciton-exiton interactions and no stimulated emission for example. Thus in the case of electron beam excitations, and using for $g(x)$ the empirical expression of Philibert,[17] the calculation of $A(\alpha)$ is straightforward and yields the following results[18]: *the curve $A(\alpha)$ is independent of the excitation intensity, $A_{\max}$ and A_∞ decrease when the excitation depth increases and the ratio $A_{\max}/A_\infty$ increases with the excitation depth.*

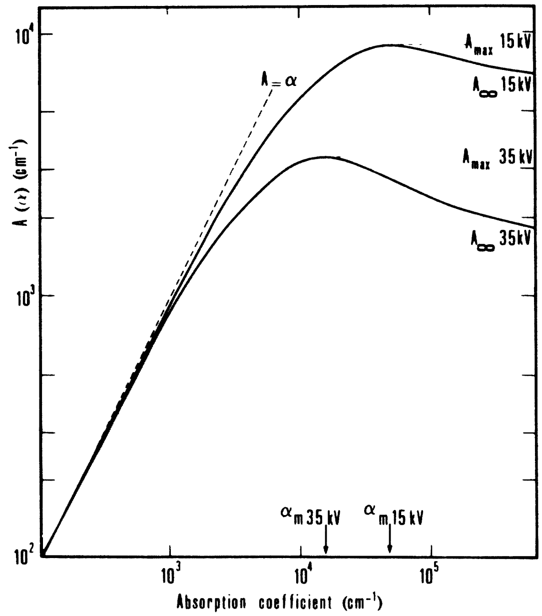

FIG. 1. Typical $A(\alpha)$ curves for two energies of the electron beam (35 and 15 kV). These curves have been calculated for the following values of the parameters: $\rho = 5.8$; $L = 0.5$ μm; $S = 10^4$ cm/sec; $D = 0.25$ cm^2/sec; $\tau = 10^{-8}$ sec. Note that α_m is defined in Appendix A.

These results are illustrated in Fig. 1, where $A(\alpha)$ is calculated in a typical case using[18] Eqs. (B1) and (B3) for two different energies of the electron beam. Knowing $A(\alpha)$, the $A(h\nu)$ spectrum can be determined from the absorption spectrum $\alpha(h\nu)$. This is illustrated in Fig. 2. In quadrant (a) we have drawn a schematic and arbitrary absorption spectrum with two lines (I, II) of different intensities and a band-to-band absorption edge[19] (III). The peaks I and II correspond respectively to weak and strong exciton absorptions. In quadrant (b), we have represented the $A(\alpha)$ curves given in Fig. 1. The $A(h\nu)$ spectra [quadrant (c)] are obtained from quadrants (a) and (b) as follows. For each value of the energy $h\nu$, quadrant (a) gives α. Then, from quadrant (b) one can obtain $A(h\nu)$ whose behavior is given in quadrant (c). From the results given in quadrant (c), we see that a rather small absorption peak like I ($\alpha d < 1$) yields a peak in the $A(h\nu)$ spectrum, the intensity of which decreases when the excitation depth increases which means that we have a small reabsorption. On the contrary an intense absorption peak like II yields a dip in the $A(h\nu)$ spectrum whose depth increases with the electron beam energy. *The bottom of the dip corresponds to the energy of the maximum of the absorption peak.* Therefore, in the case of strong excitonic absorption, the energy of the dip in the $A(h\nu)$ spectrum gives the exciton energy. Note that this shape is only due to the fact that near the sample surface the exciton density profile increases from the surface to the bulk. (This is not surprising because it is exactly the same phenomenon as the inversion of spectral lines in the spectroscopy of gases.[20]) In the case of an electron beam excitation, this condition is satisfied as shown in Ref. 21. In the case of a laser beam excitation, this condition requires a strong recombination at the surface of the sample and a diffusion length [see Eq. (6)] not too large compared to the penetration of the laser beam. We want to emphasize that the principle of the theoretical model described here has been first proposed by Noblanc *et al.*[4] However these authors did not take into account the diffusion and the surface recombination of excitons. This led them to different conclusions which could not explain our experimental data.

IV. EXPERIMENTAL RESULTS

A. $AgGaSe_2$

This compound is one of the I-III-VI$_2$ family and crystalizes in the chalcopyrite structure. Its band structure at the Brillouin-zone center is given by the quasicubic model.[22,23] There are three transitions at $k = 0$ between the valence and the

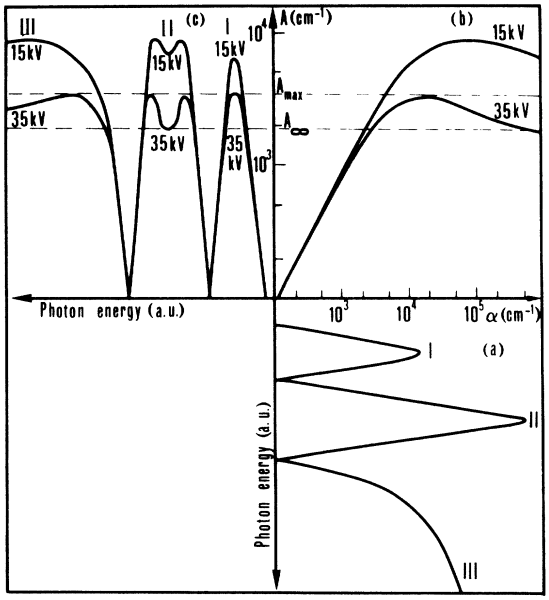

FIG. 2. Graphic determination of the $A(h\nu)$ spectrum for two arbitrary absorption lines of different intensities (I and II) and a band-to-band absorption edge (III). Quadrant (b) is a reproduction of Fig. 1.

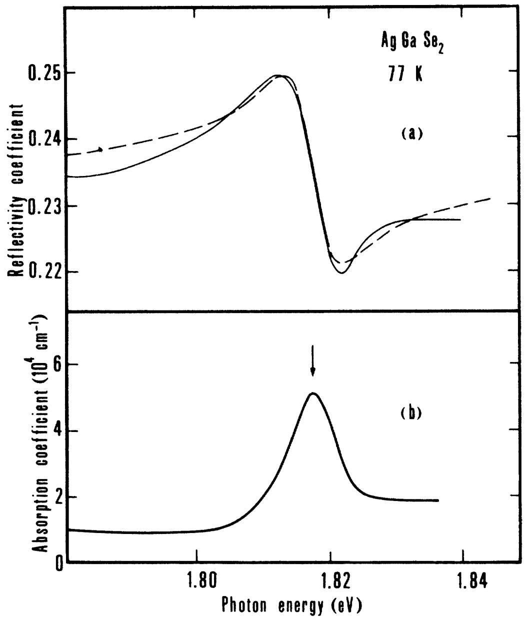

FIG. 3. (a) Comparison of the experimental reflectivity in polarization parallel to the optical axis (solid curve) to a theoretical fit (dashed line) done using a simple damped oscillator (see text). (b) Absorption spectrum obtained with the help of Kramers-Krönig relations. The arrow indicates the free-exciton energy obtained from reflectivity.

conduction bands, whose intensities depend on the polarization of the radiation relatively to the optical axis: A, which corresponds to the band gap and is more intense in parallel than in perpendicular polarization, B which is allowed only in perpendicular polarization, and C which is more intense in perpendicular polarization. Note that the notations used here are those of Ref. 22.

Figure 3(a) shows our reflectivity data in parallel polarization at 77 K. The absorption spectrum calculated from the reflectivity with the help of Kramers-Krönig relations is presented in Fig. 3(b) and exhibits a peak whose maximum is at 1.818 eV. We believe that this peak is due to free excitons. Indeed this result is in rather good agreement with previous measurements done by Tell *et al.*[23] who have obtained from reflectivity experiments 1.817 eV for the energy of the $n = 1$ free exciton at liquid-nitrogen temperature. From Fig. 3(b), we get the absorption coefficient at the free-exciton energy which is 5×10^4 cm^{-1}. Figure 3(a) shows also a least-squares fit of the reflectivity accident with a simple damped oscillator.[2,23] The long-wavelength reflectivity is taken to be 0.235 as estimated from room-temperature refractive index measurements.[24] The best fit is obtained for the following values of the parameters: the oscillator energy $E_0 = 1.818$ eV, the oscillator strength $4\pi\beta = 5.8 \times 10^{-3}$ and the damping constant $\Gamma = 8$ meV. We have also measured at 77 K the absorption coefficient in the range 10–600 cm^{-1} in parallel and perpendicular polarizations on a 100-μm thick platelet of the same ingot. These results are shown in Fig. 4. The ratio of the absorption coefficients $(\alpha_{\parallel}/\alpha_{\perp})$ is about 10, in good agreement with the measurements of Tell *et al.*[23] Therefore the absorption coefficient for the free-exciton energy in perpendicular polarization must be around 5×10^3 cm^{-1}. The penetration depth of the electron beam varying between 0.1 μm for 7 kV and 1.4 μm for 35 kV [from Eq. (B2)], we can predict that the free-exciton luminescence will be weakly reabsorbed in perpendicular polarization and strongly in the parallel one.

We have reproduced in Fig. 5 the cathodoluminescence spectra in the free-exciton energy region for parallel and perpendicular polarizations. These spectra were obtained at 77 K for different electron beam energies. It can be noted that the main luminescence peak is progressively deformed from the spectrum in perpendicular polarization obtained with a 7-keV electron beam [7 kV(⊥)] to the 30-kV(‖) spectrum. This luminescence peak shifts from 1.818 to 1.807 eV and its width increases. From these spectra, we have calculated $A(h\nu)$ using Eq. (3) and our absorption,

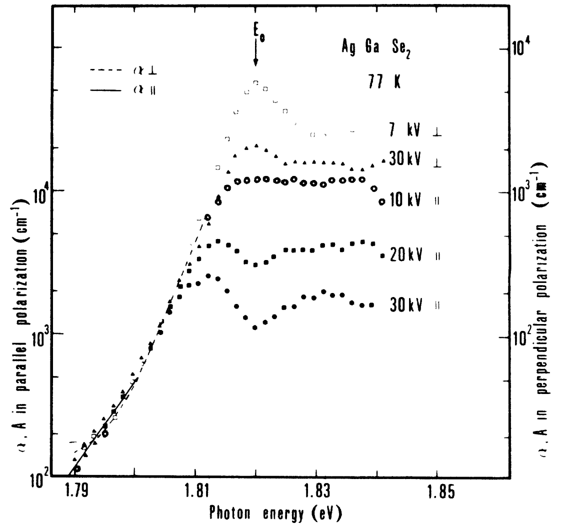

FIG. 4. $A(h\nu)$ and absorption (solid and dashed lines) spectra in parallel and perpendicular polarizations. $A(h\nu)$ is given for different energies of the electron beam. Note that ⊥(‖) corresponds to radiation polarized perpendicularly (parallely) to the optical axis.

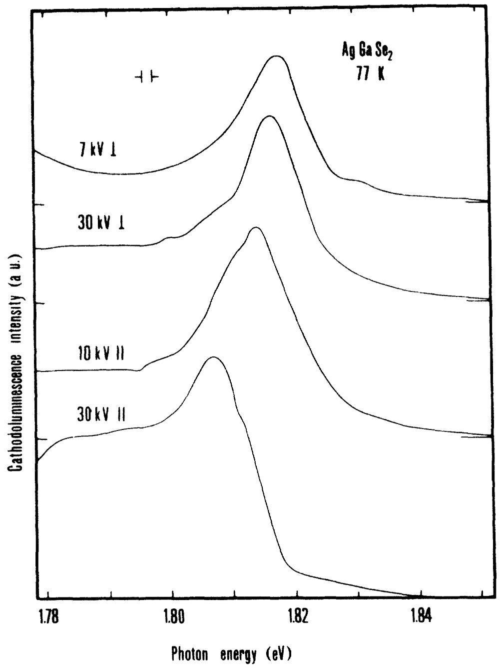

FIG. 5. Cathodoluminescence spectra of $AgGaSe_2$ at 77 K for polarizations parallel and perpendicular to the optical axis and for different energies of the electron beam.

reflectivity, and luminescence data corrected by the photomultiplier response. The $A(h\nu)$ spectra shown in Fig. 4 have been normalized so that they coincide with the absorption coefficient measured directly between 1.79 and 1.81 eV. We have seen previously that when reabsorption is negligible ($\alpha d \ll 1$), $A(h\nu)$ is equal to $\alpha(h\nu)$. This is the case of the 7-kV ($\perp$) spectrum ($\alpha d \simeq 0.1$) which presents a peak at 1.820 eV corresponding certainly to free excitons. The maximum of $A(h\nu)$ is about 6×10^3 cm^{-1}, in good agreement with the results obtained from reflectivity by the Kramers-Krönig transformation. However the energy of the $A(h\nu)$ maximum is slightly shifted towards high energies with respect to our reflectivity data, but at the moment we do not have any explanation to propose for this discrepancy. In agreement with our theoretical model, it is observed that, when the reabsorption becomes larger, the peak at 1.820 eV becomes smaller and is finally transformed in a dip whose depth increases with the electron beam energy. Besides, the theoretical results obtained in Sec. III are well illustrated by the 20 and 30 kV ($\parallel$) $A(h\nu)$ spectra: (i) $A_{\max}$ and A_∞ are smaller at 30 kV than at 20 kV, (ii) $A_{\max}/A_\infty$ is larger at 30 kV than at 20 kV. One can also notice that in the 7 kV ($\perp$) $A(h\nu)$ spectrum, there seems to be a little bump near 1.832 eV. We interpret it tentatively as the $n=2$ free exciton.[23] From this study, we conclude that the variation of the position and of the shape of the exciton peak in the luminescence spectra reported here (Fig. 5) are actually due to reabsorption.

B. $CuGaS_2$

This I-III-VI_2 compound has the same band structure than $AgGaSe_2$. However the polarization ratio, the oscillator strength and the absorption coefficient in parallel polarization for the A transition are larger than in the case of $AgGaSe_2$.[25]

From reflectivity, absorption, and luminescence experiments at 77 K, we have determined $A(h\nu)$ in parallel and perpendicular polarizations using the same procedure as in the case of $AgGaSe_2$. The results obtained in perpendicular polarization are shown in Fig. 6(a). According to Tell *et al.*,[25] the absorption coefficient for the exciton energy in perpendicular polarization does not exceed 1500 cm^{-1}, so that there is no reabsorption and $A(h\nu)$ represents the absorption spectrum. We observe perfectly the $n=1$ free exciton[25] at 2.4995 ± 0.0004 eV and the $n=2$ one at 2.524 eV. Thus assuming an hydrogenoid model, the exciton binding energy is 32 meV. Tell *et al.*[25] obtained from reflectivity measurements $E_0 = 2.499$ eV and $R_0 = 29$ meV. It is noteworthy that the absorption spectrum obtained directly on a similar crystal fits well with the $A(h\nu)$ spectrum which shows that the excitons are thermalized at 77 K. Figure 6(b) gives $A(h\nu)$ in parallel polarization for different energies of the electron beam. As in $AgGaSe_2$, the $A(h\nu)$ spectrum presents a dip which is located at 2.5015 ± 0.0008 eV and whose depth increases with the electron beam energy. Reabsorption is thus an important effect in this case but contrarily to what could be expected, the energy of the dip is not exactly the same as the one of the peak in perpendicular polarization. It is shifted by a quantity $\Delta E = 2$meV about towards high energies. This shift could be explained by a difference between the energies of the Γ_5 exciton allowed in perpendicular polarization and the Γ_4 exciton allowed in the parallel one.[26,27] However we do not think that this explanation is likely for two reasons: (i) the energy of the exciton in perpendicular polarization (obtained here from luminescence measurements) is the same than in parallel polarization[25]; (ii) we have also observed in cubic ZnSe that the energy of the dip is at a slightly higher energy than that of the exciton (see Sec. IV C1).

On the other hand ΔE seems to correspond to the longitudinal transverse exciton splitting Δ_{LT}.

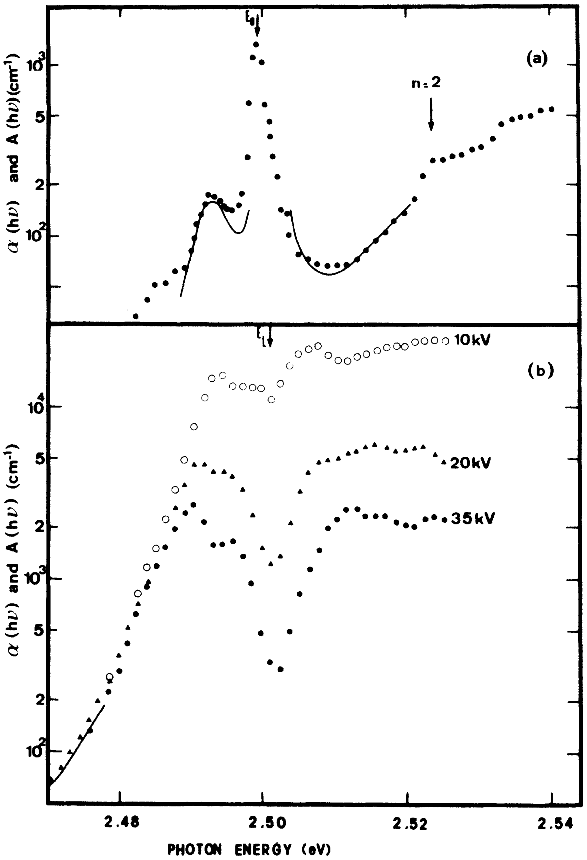

FIG. 6. $CuGaS_2$ at 77 K. Absorption (solid lines) and $A(h\nu)$ spectra in polarization (a) perpendicular and (b) parallel to the optical axis. The arrows indicate the positions of the $n=1$ transverse (E_0) and longitudinal (E_L) excitons and of the $n=2$ exciton.

Let E_L and E_T be the longitudinal and transverse exciton energies at $k=0$ and ϵ' the dielectric constant far from the exciton energy,

$$\Delta_{LT}=E_L-E_T=2\pi\beta E_T/\epsilon' . \qquad (7)$$

Taking $E_T=E_0=2.5$ eV, $4\pi\beta=0.015$,[25] and $\epsilon'=8.5$,[25] we get $E_L-E_T=2.2$ meV which is close to the difference we observe between the energies of the peak in perpendicular polarization and of the dip in parallel polarization. Besides the energy of the reflectivity minimum which is generally considered as that of the longitudinal exciton[2] is situated at 2.5015 eV like the dip in the $A(h\nu)$ spectrum. Thus the dip in the $A(h\nu)$ spectra, i.e., the maximum of reabsorption, is close to the energy of the longitudinal exciton. In fact this result is not very surprising. Indeed, as shown by Tait and Weiher[28] from calculations of the excitonic absorption spectrum in CdS done in the formalism of polaritons, the absorption coefficient can be maximum at the energy of the longitudinal exciton. As pointed out by these authors, this theoretical result is consistent with optical data obtained in different materials. We can guess that this phenomenon will be visible[26] only if Δ_{LT} is not much smaller than the width of the exciton peak Γ. In the case of $CuGaS_2$, $\Gamma\sim 2$ meV [from $A(h\nu)$ in perpendicular polarization] and $\Delta_{LT}=2.2$ meV. On the contrary in the case of $AgGaSe_2$ the peaks are wide ($\Gamma\sim 8$ meV) and the splitting is small ($\Delta_{LT}\sim 0.66$ meV with $4\pi\beta\sim 5.8\times 10^{-3}$ and $\epsilon'\sim 8$). Therefore it is not surprising that we have not observed this effect in this compound.

C. ZnSe

The optical properties of this material are better known than those of the ternary compounds. Particularly its luminescence has been extensively investigated by different authors.[29] We wish to present here the results of a study which we have also performed to investigate the influence of reabsorption on the free exciton radiation spectrum in this compound.

1. Liquid-nitrogen temperature

From absorption, reflectivity, and luminescence experiments, we have calculated as previously the $A(h\nu)$ spectra shown in Fig. 7. It can be seen that these spectra exhibit a camel back shape with a dip increasing with the excitation depth. This dip occurs at 2.7936 ± 0.0004 eV and is shifted towards high energy compared to the exciton energy obtained from electroreflectance measure-

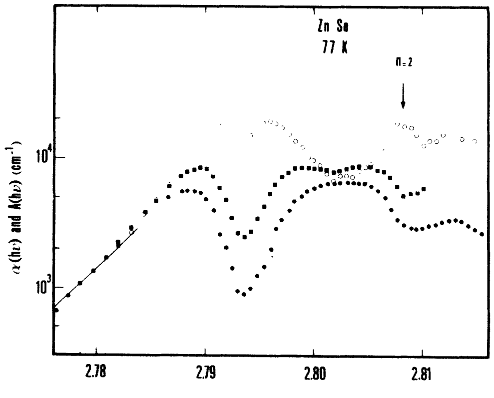

FIG. 7. Absorption spectrum obtained from direct measurements (solid line). $A(h\nu)$ spectra for different kinds of excitations: ○ He-Cd laser; ■ electron beam 20 kV; ● electron beam 30 kV.

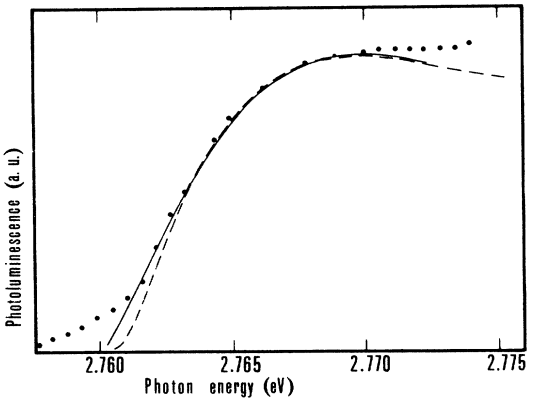

FIG. 8. Photoluminescence spectrum of the LO-phonon replica of the exciton line in ZnSe at 77 K. The dotted line gives the experimental data. The dashed line represents calculations done in the polariton model and the solid line the exciton model (see text).

ments.[30] We have observed the same kind of effect in $CuGaS_2$, and it is thus interesting to obtain a precise value of the transverse exciton energy in our samples. We have fitted in the exciton and polariton formalisms the luminescence line shape of the exciton LO phonon replica shown in Fig. 8. Both models and the values of the parameters we used are, respectively, given in Sec. IV C2. The results are given in Fig. 8. The energy of the LO phonon at the center of the Brillouin zone being 31.7 meV,[31] we obtain for the transverse exciton energy 2.7924 ± 0.0004 eV in the polariton model and 2.7918 ± 0.0004 eV in the exciton one. The exciton dip in the $A(h\nu)$ spectrum is thus shifted towards high energy with respect to the transverse exciton by 1.2 meV (polariton model) or 1.8 eV (exciton model). Thus it is quite clear that the dip in the $A(h\nu)$ spectrum occurs near the energy of the longitudinal exciton. Indeed, with $4\pi\beta = 6.1 \times 10^{-3}$,[32,33] and $\epsilon' = 7.7$,[34] the longitudinal transverse splitting is $\Delta_{LT} = 1.1$ meV. This is quite comparable to what happens in $CuGaS_2$ and can certainly be interpreted as in the case of this ternary compound.

From Sondergeld and Stafford[35] measurements, the binding energy of the free exciton is 20 ± 0.7 meV which gives 2.807 eV for $n = 2$ exciton energy. In fact we observe in the $A(h\nu)$ spectra a peak in the case of laser beam excitation and a well shaped dip in the case of electron beam bombardement near 2.808 eV that we attribute to the $n = 2$ exciton. This corresponds to a binding energy of the exciton of 21 meV. The $n = 2$ peak does not present a dip in the $A(h\nu)$ spectrum corresponding to laser excitation certainly because the absorption coefficient is not large enough. Finally, in view of the study presented in this section, we believe that the excitation dependence of the luminescence spectra in the exciton energy region (see Fig. 9) is here also due to reabsorption.

2. Helium temperature

As shown in Fig. 10, the high-energy part of the photoluminescence spectrum at 2 K presents a succession of narrow peaks which have already been observed by other authors.[29] If we compare, for example, the relative intensities of I_1 or I_2 (bound excitons) and of E_x (free excitons) to what has been reported in previous works,[29] it is clear that the quality of our samples is very good. However, in some samples, the E_x, I_1, and I_2 peaks and their phonon replicas are wider and shifted to lower energies by the same quantity[36, 37] (from 2 to 4 meV), but all the results presented here have been obtained with samples which did not present this kind of effect. Figure 11 gives the luminescence spectra in the exciton energy region

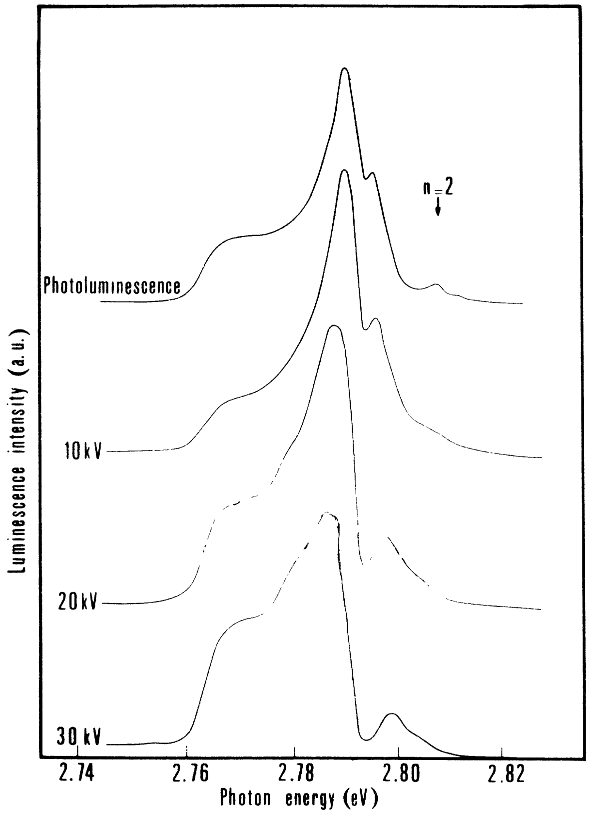

FIG. 9. Luminescence spectra of ZnSe at 77 K using different kinds of excitations (laser and electron bombardment). The arrow gives the $n = 2$ exciton position.

obtained with different conditions of excitation. We can make the following observations: (i) The peaks are wider in cathodoluminescence than in photoluminescence. This may result only from the fact that the temperature of the sample is higher in electron bombardment experiments where the sample is glued on a cold finger than in photoluminescence where it is immersed in pumped liquid helium. (ii) The shape of the free-exciton line depends strongly on the excitation intensity in cathodoluminescence: we do not see any new peak when the excitation increases (from 10^2 to 2×10^3 W/cm^2) but the free exciton peak disappears. We do not have at the present time any interpretation for this effect.

To get the $A(h\nu)$ spectrum from luminescence, one needs to know the exciton temperature because it may be rather different from that of the bath in this temperature range. To determine it we have fitted the peak at 2.770 eV, which corresponds to the LO-phonon replica of the exciton, with a theoretical expression calculated in the formalism of polaritons. Like Tait and Weiher[38] we consider that polaritons with energy $h\nu$ and wave vector k situated under the bottleneck are generated from polaritons with energy $h\nu+\Omega$ situated near the bottleneck by creation of one LO phonon with energy Ω and wave vector q. If we assume that the polaritons which are situated near the transverse exciton energy E_0 are in thermal equilibrium, the rate of generation of polaritons $P(h\nu)$ is given by

$$P(h\nu)\propto N(h\nu+\Omega)f(h\nu+\Omega)N(h\nu)\int W(q)\,dq\ , \qquad (8)$$

where $N(h\nu+\Omega)$ and $N(h\nu)$ are the densities of states of polaritons at the energies $h\nu+\Omega$ and $h\nu, f(h\nu+\Omega)$ is the number of polaritons per state, and $W(q)$ is the square of the matrix element given by Toyozawa.[39] The integral is taken over the sphere of radius k. The densities of states $N(h\nu)$ and $N(h\nu+\Omega)$ are calculated from the dispersion relation of polaritons:

$$\hbar^2c^2k^2/(h\nu)^2=\epsilon'+4\pi\beta/[1-(h\nu)^2/E_k^2]\ . \qquad (9)$$

E_k is the transverse exciton energy corresponding to wave vector k:

$$E_k=E_0+\hbar^2k^2/2m^*\ ,$$

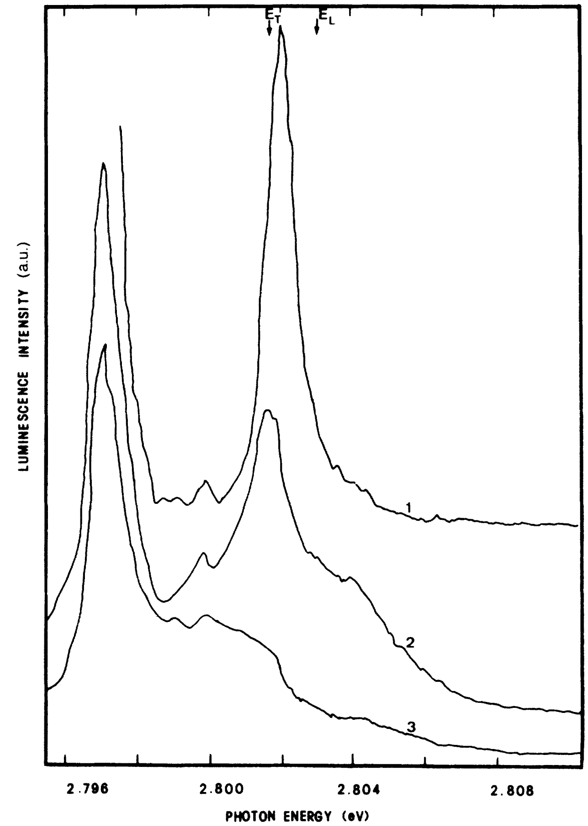

FIG. 11. Luminescence spectra of ZnSe at liquid-helium temperature for different conditions of excitation: (a) Laser beam at 3.250 Å; (b) electron beam at 30 kV (10^2 W/cm^2); (c) electron beam at 30 kV (2×10^3 W/cm^2).

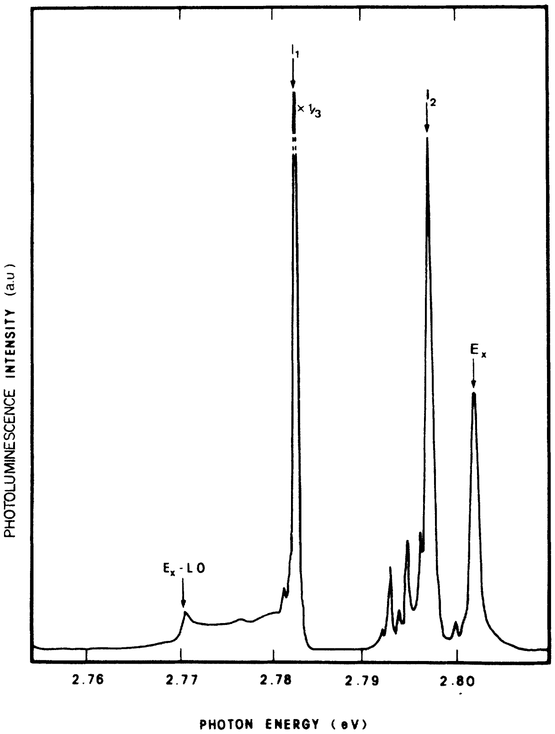

FIG. 10. Photoluminescence spectrum of ZnSe at 2 K.

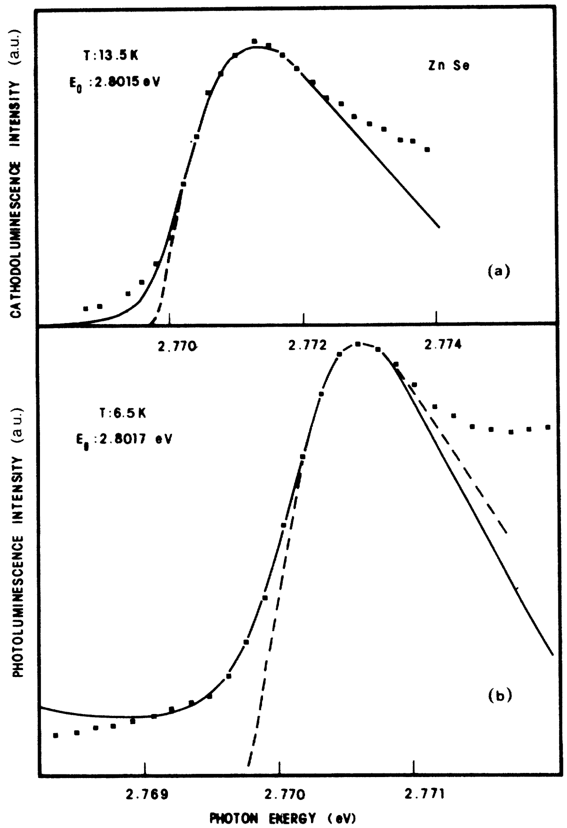

FIG. 12. Experimental (■) spectrum of the LO-phonon replica of the exciton luminescence line obtained in ZnSe at helium temperature; (a) and (b) correspond, respectively, to electron beam and laser excitations. The dashed lines give the theoretical line shape of this replica calculated in the exciton model: in (a), $E_0 = 2.8014$ eV and $T = 12.6$ K; in (b), $E_0 = 2.8014$ eV and $T = 7$ K. The solid lines correspond to calculations done in the polariton model with $m_e = 0.16\, m_0$ (Ref. 29), $m_h = 0.75\, m_0$ (Ref. 33), $\epsilon' = 7.7$ (Ref. 34) and $4\pi\beta = 0.0061$ (Ref. 32); the values of E_0 and T are given in the figure.

where $m^* = m_e + m_h$ is the exciton mass. Figure 12 represents the experimental photoluminescence and cathodoluminescence peaks and the best fits in the polariton model and in a simple exciton model where

$$I(h\nu) = (h\nu - E_0 + \Omega)^{3/2} e^{-h\nu/kT} .$$

The corresponding values of E_0 and T are given in Fig. 12. One can see that the polariton model gives better fits and seems more appropriate than the exciton one. From these data we deduce also that the polaritons are in quasithermal equilibrium over a range of 2 meV around E_0.

From the experimental reflectivity and absorption spectrum given in Fig. 13 and the luminescence data shown in Fig. 11, we have obtained the $A(h\nu)$ spectra presented in Fig. 13. Taking into account the luminescence results described above we used here the values of T given in Fig. 12 in the case of the polariton model. We note first that it is not possible to superpose the low energy part of the $A(h\nu)$ spectra on the absorption curve. However, this part of the luminescence spectrum is dominated by the recombination of excitons bound to neutral impurities. The large resistivity of the samples at room temperature[40] (10^8–10^9 Ω cm) shows that impurities are almost all compensated, so that they are all ionized during absorption measurements. On the contrary, in the luminescence experiments the sample is strongly excited and all the impurities are neutral. Therefore we believe that this may explain the discrepancy between $A(h\nu)$ and α. The second statement is that the $A(h\nu)$ spectra present a dip at 2.8030 eV which corresponds nearly to the long-

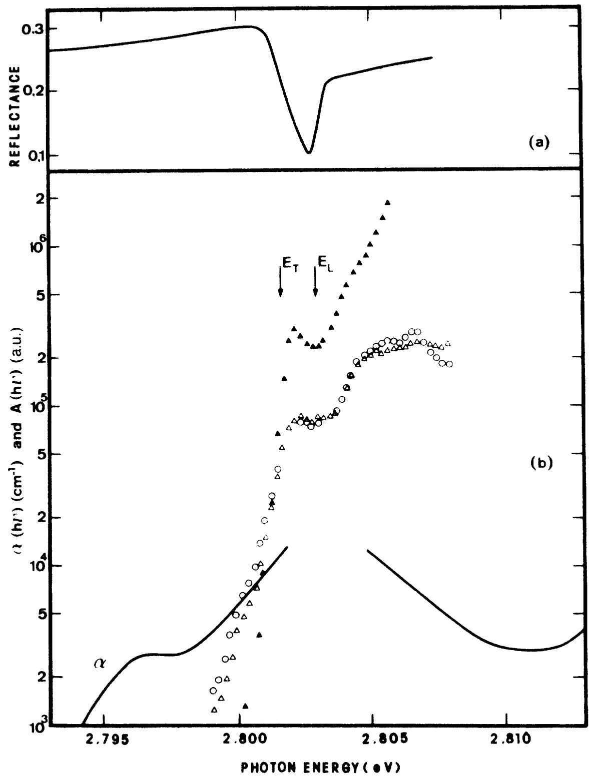

FIG. 13. ZnSe at liquid-helium temperature. (a) Reflectivity (b) $A(h\nu)$ spectra for different conditions of excitation: ▲ laser beam; ● 30-kV electron beam; △ 7-kV electron beam. The solid line gives the absorption coefficient measured directly in a thin sample (25 μm). E_L (E_T) gives the energy of the longitudinal (transverse) exciton.

itudinal exciton energy as it is the case at 77 K. However the depth of the dip does not increase with the width of the excited layer so that it is certainly not possible to interpret it in terms of reabsorption. This suggests strongly that the excitonic absorption is smaller at low temperature than at 77 K. Such a result might seem surprising but similar conclusions have been recently drawn in CdS,[41] Cu$_2$o,[42] and GaSe,[43] from direct absorption measurements. As discussed in Refs. 41–43, it seems that such an effect can only be understood in a polariton model. Therefore, from the results reported here, we are led to conclude that there are certainly strong polariton effects in ZnSe at low temperature. Finally, Sell *et al.*[41] have observed in GaAs at low temperature (2 K) a doublet structure in the exciton luminescence spectrum. These authors have attributed the low-energy peak to the lower polariton branch and the upper one to the upper polariton branch. Calculations of $A(h\nu)$ from the results of Ref. 44 lead to $A(h\nu)$ spectra whose shape is similar to ours. Therefore, in view of our results, we think that in ZnSe the low-energy peak at 2.8022 eV in the $A(h\nu)$ spectrum is due to the lower polariton branch whose population is in thermal equilibrium between 2.801 and 2.803 eV as seen previously. We suggest that the large increase of $A(h\nu)$ above 2.803 eV may be due to the upper polariton branch.

V. CONCLUSION

To summarize, using a simple and new theoretical model to analyze our luminescence data in AgGaSe$_2$, CuGaS$_2$, and ZnSe, we have shown that reabsorption is generally not negligible in the excitonic luminescence observed at 77 K in these materials. The method presented here to study reabsorption yields also the free-exciton energy and is obviously applicable to other direct-band-gap materials. Of course this method is only interesting when the absorption coefficient is large in the exciton energy region. It is noteworthy that in CuGaS$_2$ and in ZnSe our model gave us the longitudinal exciton energy because it happens that in these cases the absorption is maximum at this energy. This can be understood from the theory of Tait and Weiher.[28]

In addition, we deduce from our investigations that in ZnSe at liquid-helium temperature there is practically no reabsorption of the light emitted in the excitonic part of the spectrum. We believe that this means that polariton effects are important in this material at low temperature. This conclusion is supported by previous studies performed in CdS,[41] Cu$_2$O,[42] and GaSe.[43]

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APPENDIX A

To describe the behavior of $A(\alpha)$ when α tends to infinity we develop first $n(x)$ in the vicinity of the surface $(x=0)$:

$$n(x)=n(0)+x\,\frac{\partial n(0)}{\partial x}+xO(x)\,.$$

Using Eq. (5), this yields

$$n(x)=n(0)(1+xS/D)+xO(x)\,.$$

The Laplace transform of $n(x)$ is thus

$$H(\alpha)=\frac{1}{\alpha}n(0)+\frac{1}{\alpha^2}\,\frac{S}{D}n(0)+\frac{1}{\alpha^2}\,O\left(\frac{1}{\alpha}\right)$$

and

$$A(\alpha)=\frac{n(0)}{H(0)}+\frac{1}{\alpha}\,\frac{S}{D}\,\frac{n(0)}{H(0)}+\frac{1}{\alpha}\,O\left(\frac{1}{\alpha}\right)\,.$$

The coefficient of $1/\alpha$ being positive, $A(\alpha)$ approaches a limit A_∞ by decreasing values when α tends to infinity. $A(\alpha)$ being proportional to α for the small values of α, it has a maximum $A_{\max}$ for a finite value α_m of α.

APPENDIX B

To obtain $A(\alpha)$ in cathodoluminescence as a function of the electron beam energy, we start from Eq. (4) which yields easily

$$\begin{aligned}H(\alpha)&=\int_0^\infty n(x)e^{-\alpha x}\,dx\\&=\frac{\tau[n(0)(\alpha D+S)-G(\alpha)]}{\alpha^2L^2-1}\,,\end{aligned}$$

where $G(\alpha)$ is the Laplace transform of $g(x)$, τ the exciton lifetime, and $L=(D\tau)^{1/2}$. Since $H(\alpha)$ cannot be infinite for $\alpha=1/L$, we obtain the following condition:

$$n(0)=\frac{G(1/L)}{(D/L)+S}\,.$$

Finally we get

$$\begin{aligned}A(\alpha)&=\frac{H(\alpha)}{H(0)}\\&=\alpha\,\frac{G(1/L)(LS+\alpha LD)-(LS+D)G(\alpha)}{[G(1/L)LS-(LS+D)G(0)](1-\alpha^2L^2)}\,.\end{aligned}\qquad\text{(B1)}$$

In cathodoluminescence, the generation profile is given by the Philibert[17] formula

$$G(x)=KVI(1+h)\sigma\rho(e^{-\sigma\rho x}-e^{-(1+1/h)\sigma\rho x}), \qquad \text{(B2)}$$

where $h=1.2\sum_i C_i(M_i/Z_i^2)$, $\sigma=4.5\times10^5/V^{1.65}$ in cm^{-1}, ρ is the density of the material, V is the energy of the electron beam in keV, I is the intensity of the electron beam, C_i, Z_i, M_i are the concentrations, atomic numbers, and atomic masses of the different atoms constituting the sample, and K is a constant which is approximately equal to $1/2E_G$ if E_G is the band gap. The Laplace transform of $g(x)$ is

$$G(\alpha)=G(0)/(\alpha a+1)(\alpha\gamma a+1), \qquad \text{(B3)}$$

where $a=1/\sigma\rho\propto V^{1.65}$ and $\gamma=h/(1+h)$. Let us examine at first the variation of $G(\alpha)$ with the energy of the electron beam:

$$\frac{\partial}{\partial V}\left(\frac{G(\alpha)}{G(0)}\right)=-\frac{\alpha(2\alpha\gamma a+\gamma+1)}{(\alpha a+1)^2(\alpha\gamma a+1)^2}\,\frac{\partial a}{\partial V}<0\,.$$

$G(\alpha)/G(0)$ is thus a decreasing function of the energy of the electron beam. When the absorption coefficient tends towards infinity, it is shown in Appendix A that $A(\alpha)$ tends towards a limit

$$A_\infty=\frac{n(0)}{H(0)}=\frac{LG(1/L)/G(0)}{\tau[D+LS-LSG(1/L)/G(0)]}\,. \qquad \text{(B4)}$$

Equation (B4) shows that A_∞ is an increasing function of $G(1/L)/G(0)$; it is thus a decreasing function of the energy of the electron beam.

Let us study now the variation of $A(\alpha)/A_\infty$:

$$\frac{A(\alpha)}{A_\infty}=\frac{\alpha\tau(\alpha D+S)}{\alpha^2L^2-1}-\frac{\alpha L(LS+D)G(\alpha)}{D(\alpha^2L^2-1)G(1/L)}\,,$$

$$\frac{\partial}{\partial V}\,\frac{A(\alpha)}{A_\infty}=\frac{\alpha(D+LS)[(1+\gamma)(L+\alpha\gamma a^2)+2\gamma a(1+\alpha L)]}{DL(\alpha L+1)(\alpha a+1)^2(\alpha\gamma a+1)^2}\,\frac{\partial a}{\partial V}\,.$$

Therefore $A(\alpha)/A_\infty$ increases with a and increases with the energy of the electron beam. *A fortiori*, the behavior of $A_{\max}/A_\infty$ will be the same.

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