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Thermal activation of localized excitons in $Zn_xHg_{1-x}Te$ semiconductor alloys: Photoluminescence line-shape analysis

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Photoluminescence spectra of $Zn_xHg_{1-x}Te$ semiconductor alloys (and of other II–VI alloys) show that the line due to excitons localized by composition disorder shifts to higher photon energy with increasing temperature. This blueshift is attributed to the thermal activation of localized excitons within the density-of-states tail. By incorporating this process into a theoretical model previously developed for the low-temperature situation, a good agreement with the experiments is obtained.

I. INTRODUCTION

Localization of excitons due to potential fluctuations in semiconductor alloys has been extensively studied in the past years.[1–3] Most of the information has been extracted from the analysis of low-temperature photoluminescence spectra, measured under continuous or transient excitation.[4,5] We have recently reported on exciton localization occurring in Zn-rich $Zn_xHg_{1-x}Te$ alloys.[6–8] A simple model for the density of localized states was given which allowed us to fit the low-temperature photoluminescence line shape in ZnHgTe but also in CdSSe and CdHgTe alloys.[9]

We present here an extension of this model able to cover the exciton behavior at finite temperatures where thermally activated transitions between localized states have to be taken into account. In the following we describe photoluminescence spectra measured on a $Zn_{0.97}Hg_{0.03}Te$ crystal as a function of temperature and we make a comparison with the results of the theoretical analysis. The good agreement observed constitutes an additional check of the validity of our simple model of tail states.

II. EXPERIMENTS

The sample used for this study was cut from a crystal grown by traveling heater method (THM), using Te as the solvent.[10] The luminescence was excited with a focused 488-nm beam from a 10-mW Ar^+ laser, analyzed with a 60-cm Jobin-Yvon double monochromator and detected by a GaAs photomultiplier.

Figure 1 presents a series of luminescence spectra measured at different temperatures on a $Zn_{0.97}Hg_{0.03}Te$ sample. The low-temperature luminescence spectrum (2 K) shows a single intense line (L) with asymmetric shape due to excitons localized in a tail derived from disorder-induced potential fluctuations.[7,8] The line peak is at 5.7 meV below the free exciton energy measured by reflectivity. From 2 K up to about 20 K, this line shifts smoothly to higher energies and beyond 20 K it follows the variation of the band gap, shifting to lower energies. With increasing temperature, the line (L) becomes broader and takes a symmetrical shape; its intensity decreases.

Such temperature dependence of the luminescence spectrum has already been reported in a few semiconduc-

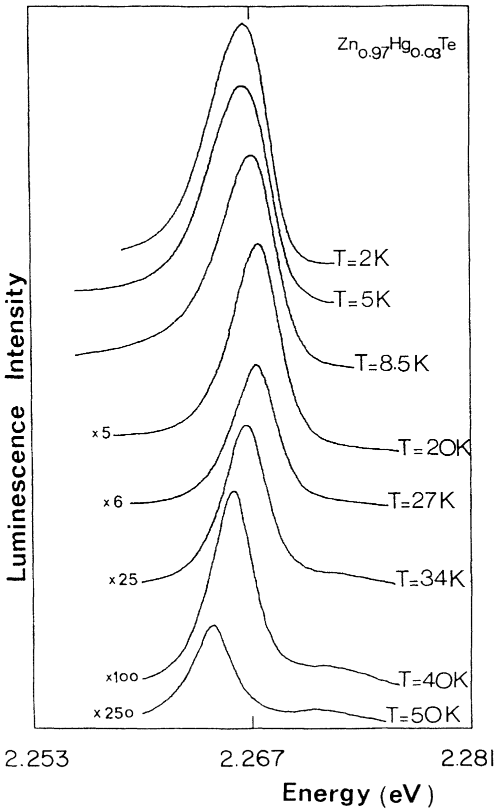

FIG. 1. Temperature evolution of the $Zn_{0.97}Hg_{0.03}Te$ luminescence spectrum.

tor alloys like $Zn_xCd_{1-x}S$ $(x<0.15)$,[11] $Zn_xCd_{1-x}Se$ $(0.8<x<1)$,[12] and $Cd_xHg_{1-x}Te$ $(0.6<x<1)$.[13]

III. THEORETICAL ANALYSIS

The observed behavior as a function of temperature can be analyzed in the frame of exciton transfer between localized states in the density-of-states tail (Fig. 2). We consider a steady-state nonresonant type of excitation: photons of energy higher than the semiconductor band gap contribute to establish a population of free excitons of density n_0, from which capture to localized states proceeds. In the small-excitation regime and at low temperatures, the calculation of the density of localized excitons at energy ε below the free exciton energy, $n(\varepsilon)$, was previously treated by using a phenomenological model of transfer recombination.[9] With rising temperature, excitons are transferred to higher energies by acoustical-phonon absorption (thermal activation). Extension of the low-temperature model is made by including two terms labeled (A_2) and (A_1) (Fig. 2). They represent the variation of the localized exciton population at energy ε, due to thermal activation from deeper localized states $(\varepsilon''>\varepsilon)$, and to emission towards shallower localized states $(\varepsilon'<\varepsilon)$, respectively. In the small-excitation regime, the density of localized excitons at energy ε and temperature T satisfies the rate equation,

$$\beta n_0 g(\varepsilon)+\sum_{\varepsilon'=0}^{\varepsilon}\omega_{\varepsilon'\to\varepsilon}(\varepsilon,\varepsilon')n(\varepsilon')-\sum_{\varepsilon''=\varepsilon}^{+\infty}\omega_{\varepsilon\to\varepsilon''}(\varepsilon,\varepsilon'')n(\varepsilon)-\sum_{\varepsilon'=0}^{\varepsilon}\omega'_{\varepsilon\to\varepsilon'}(\varepsilon,\varepsilon')n(\varepsilon)+\sum_{\varepsilon''=\varepsilon}^{+\infty}\omega''_{\varepsilon''\to\varepsilon}(\varepsilon,\varepsilon'')n(\varepsilon'')-\frac{n(\varepsilon)}{\tau_R}=0\,, \tag{1}$$

with

$$g(\varepsilon)=g_0\exp-\{\varepsilon/\varepsilon_0\}^{3/2}\,,$$
$$\omega_{\varepsilon'\to\varepsilon}(\varepsilon,\varepsilon')=\omega_0(\varepsilon')g(\varepsilon)\,, \tag{2}$$
$$\omega_0(\varepsilon)=\frac{\exp\{\delta(\varepsilon_M-\varepsilon)\}}{\tau_R\int_0^{\varepsilon}g(\varepsilon')d\varepsilon'}\,.$$

β is the capture coefficient of free excitons on the localized states of density $g(\varepsilon)$. The energy dependence $g(\varepsilon)$ is expressed according to the previous model.[9] The probability of transfer ω is proportional to the density of final states $g(\varepsilon)$ and to a phenomenological coefficient ω_0.[14] ε_M and δ are fitting parameters and τ_R is the radiative lifetime assumed to be independent of energy.

The probability coefficients ω' and ω'' corresponding to the (A_1) and (A_2) processes, respectively, are expressed as a function of the capture probability ω [Eq. (2)] by using the Shockley-Read model which describes the capture-emission transitions in a two-level system:[15]

$$\omega'_{\varepsilon\to\varepsilon'}(\varepsilon,\varepsilon')=\omega_0(\varepsilon')g(\varepsilon')\exp\left\{-\frac{(\varepsilon-\varepsilon')}{k_BT}\right\}\,,$$
$$\omega''_{\varepsilon''\to\varepsilon}(\varepsilon,\varepsilon'')=\omega_0(\varepsilon)g(\varepsilon)\exp\left\{-\frac{(\varepsilon''-\varepsilon)}{k_BT}\right\}\,. \tag{3}$$

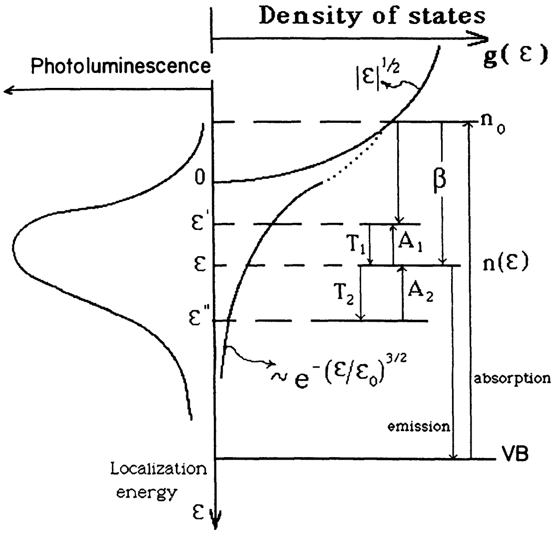

FIG. 2. Schematic representation of the excitonic transitions.

Introducing the effective exciton lifetime

$$\tau(\varepsilon)=\frac{\tau_R}{1+\exp[\delta(\varepsilon_M-\varepsilon)]+\int_0^{\varepsilon}\omega'_{\varepsilon\to\varepsilon'}(\varepsilon,\varepsilon')d\varepsilon'}$$

and replacing the summation by an integral allows us to write (1) in the form

$$\frac{n(\varepsilon)}{\tau(\varepsilon)}=\beta n_0 g(\varepsilon)+\int_0^{\varepsilon}\omega_{\varepsilon'\to\varepsilon}(\varepsilon,\varepsilon')n(\varepsilon')d\varepsilon' +\int_{\varepsilon}^{\infty}\omega''_{\varepsilon''\to\varepsilon}(\varepsilon,\varepsilon'')n(\varepsilon'')d\varepsilon''\,. \tag{4}$$

To obtain the T dependence of the luminescence intensity at energy ε, which varies as $n(\varepsilon)/\tau_R$, the integral equation (4) was solved numerically. The parameters ε_0, ε_M, and δ determined in the low-temperature study for the same sample were used[9] (Table I). Figure 3 shows calculated spectra for different values of k_BT ($k_B=0.086$ meV K^{-1} is the Boltzmann constant).

IV. DISCUSSION AND CONCLUSION

Similarly to the experimental results (Fig. 1), the peak positions of the calculated spectra shift to higher energies (smaller ε) with increasing temperature. Quantitatively,

TABLE I. Best parameters used for the fit of the low-temperature luminescence spectrum.

$Zn_{0.97}Hg_{0.03}Te$	
ε_0 (meV)	4.8
δ (meV^{-1})	1.23
ε_M (meV)	4.7

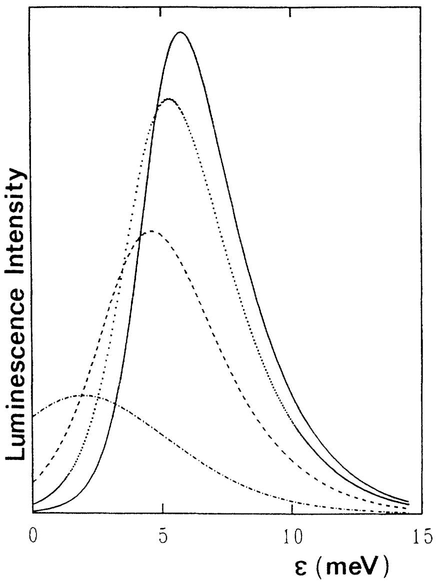

FIG. 3. $Zn_{0.97}Hg_{0.03}Te$ luminescence spectra calculated for different values of $k_B T$ (meV): ——, 0; · · · ·, 0.5; — — —, 0.9; —·—·—·, 1.5.

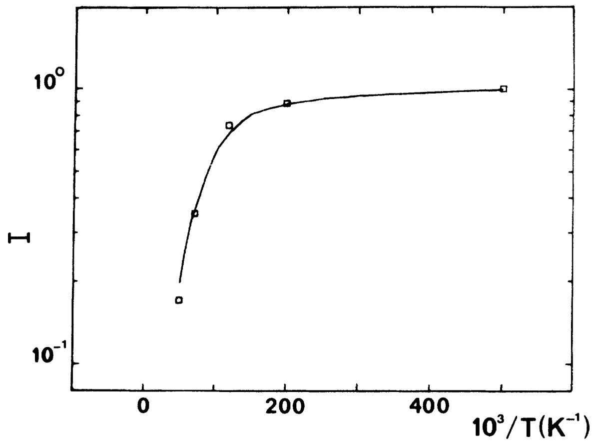

FIG. 4. Variation of the luminescence intensity with temperature: comparison between the calculated peak intensity (——) and the experimental values (☐).

the theoretical shift is 5 meV between 2 and 20 K, while the experimental shift is 1.5 meV only. This difference is mainly due to the variation of the band gap with temperature. Indeed, the energy gap decreases by 2 meV in the same temperature range. With this correction, the calculated shift of the luminescence line amounts to 3 meV, closer to the experimental value.

On the other hand, our model reproduces very well the variation of the luminescence intensity with temperature, as illustrated in Fig. 4 which compares the calculated peak intensity with the experimental values.

In conclusion, our analysis based on the thermally assisted delocalization of excitons is able to describe the blueshift with increasing temperature of the exciton-related luminescence line. The agreement between the theoretical predictions and the experimental results obtained on a $Zn_{0.97}Hg_{0.03}Te$ crystal is fair. This gives good support to the model of density of localized states derived previously.[9] A more refined analysis would have to include second-order effects such as the energy dependence of the radiative lifetime. On the other hand, the present formulation could be easily adapted to the study of high-excitation effects[16] by taking into account the partial filling of the final states involved in the various transitions.

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