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Temperature shift of the emission edge in ZnS and CdS

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The temperature dependence of the position of the edge-emission-band maximum can be explained as being due to the effect of phonon-generated electric microfields through the internal Franz-Keldysh effect. In ZnS between 100 and 300 K, the position of the edge-emission-band maximum can be described by $E_p(T) = E_p(0) - S'[1 - \coth(\hbar\omega_{\mathrm{LO}}/2kT)]$, where $\hbar\omega_{\mathrm{LO}} = 43.5$ meV and S' is a material constant. Quantitative comparisons for CdS are also given.

INTRODUCTION

There are two main contributions to the temperature dependence of the optical edge in semiconductors. First, the band structure is affected by the thermal expansion of the lattice; the second contribution arises from the electron-phonon interaction.[1] Dilation contribution can be calculated from the measured pressure coefficients,[2] and it usually contributes 10–20% to the temperature dependence of the gap energy.[3,4]

To account for the phonon contribution, a new approach, based on the Dow and Redfield model of internal electric microfields,[5] was proposed[6] to explain the temperature shift of exponential absorption edges in some II-VI compounds by considering the Franz-Keldysh effect of the absorption edge as due to the temperature-dependent phonon-generated microfields. For exponential absorption edges the shift of the edge ΔE_g is[7]

$$\Delta E_g = -C(\sigma/kT)^2 F^2 = -\gamma F^2\,, \tag{1}$$

where C is a constant, σ is the temperature-dependent slope parameter of the exponential absorption edge, and F is the applied electric field. This is a weak-field approximation ($F \sim 10^4$–10^6 V/cm) for direct band-to-band transitions, with the assumption of uniform electric field strength within a small (commensurable with the excitonic radius) volume of the crystal. Thus, any internal electric field which meets the above requirements of the Franz-Keldysh effect can be considered to be responsible for the absorption-edge shift. The sources of the electric microfields can vary from material to material and may involve phonons, ionized impurities, surfaces, and other defects.[5] The LO-phonon-generated mean-square field was derived by Dow and Redfield[5]:

$$\begin{aligned}\langle F^2\rangle &= \frac{\hbar\omega_{\mathrm{LO}}\, q_c^3(\epsilon_0 - \epsilon_\infty)}{3\pi\epsilon_0\epsilon_\infty}\coth\left(\frac{\hbar\omega_{\mathrm{LO}}}{2kT}\right)\\ &= \beta\coth\left(\frac{\hbar\omega_{\mathrm{LO}}}{2kT}\right),\end{aligned} \tag{2}$$

where $\hbar$, ω, k, and T have their usual meaning; ϵ_0 and ϵ_∞ are the static and optical dielectric constants, respectively; q_c is the polaron cutoff wave vector, normally of the order of π/a, where a is the exciton radius. When the requirement of the quasiuniform field in the vicinity of the exciton is introduced,[5] the wave vector q_c has to satisfy $q_c \leqslant \pi/a$. Table I summarizes the pertinent data on LO-phonon-generated microfields for ZnS and CdS.

Substituting $\langle F^2\rangle$ for F^2 in Eq. (1) and introducing the slope parameter $\sigma = \sigma_0(2kT/\hbar\omega_0)\tanh(\hbar\omega_0/2kT)$ with the assumption that only one type of phonons is involved in the process, the dependence $E_g(T) \propto \tanh(\hbar\omega_0/2kT)$ was obtained for the absorption edge.[6] It was also found[6] for ZnS that the LA phonons were effective in the temperature range between 50° and 100 °K, and the piezoelectric fields associated with these phonons were responsible for most of the temperature shift of the absorption edge; at temperatures above 100 °K the interacting fields were due to the LO phonons.

In the present work we extend this approach to the emission edges as well. There are several reasons for expecting the edge emission to behave in a similar manner as the absorption edge in the context of the present work. Recently, the external Franz-Keldysh effect was reported in the emission spectra of several semiconductors.[8-12] It was also demonstrated[13] that the internal electric microfield model could be employed to account for the shape of the edge of acceptor-to-band emission in the photoluminescence of GaAs. These suggest that the internal Franz-Keldysh effect due to the phonon-generated microfields, which was successfully applied to the absorption edges, can be extended to the case of the emission edges as well.

RESULTS

Assuming that, as in the case of absorption edges, the Franz-Keldysh shift of the position of the edge-emission-band maximum ΔE_p is propor-

TABLE I. Static (ϵ_0) and optical (ϵ_∞) dielectric constants; 1*s* exciton radius *a*; LO-phonon energies $\hbar\omega_{LO}$; the root-mean-square electric field strength F_{rms} due to LO phonons at 300°K [Eq. (2)] for values of $q_c = \pi/2a$, $3\pi/4a$, and π/a. (For data see Ref. 6).

	ϵ_0	ϵ_∞	a (Å)	$\hbar\omega_{LO}$ (meV)	$10^{-5}F_{rms}$ (V/cm) ($q_c=\pi/2a$)	$10^{-5}F_{rms}$ (V/cm) ($q_c=3\pi/4a$)	$10^{-5}F_{rms}$ (V/cm) ($q_c=\pi/a$)
ZnS	8.3	5.1	18	43.5	2.2	4.0	6.2
CdS	8.9	5.1	23	38.0	1.6	2.9	4.5

tional to F^2, and that only one type of phonon is responsible for the emission process at the position of the band maximum,[14] the phonon contribution to the temperature shift of E_p can be expressed as

$$\Delta E_p = -\gamma' F^2_{rms} , \qquad (3)$$

where γ' is the Franz-Keldysh coefficient for the position of the emission band maximum and F_{rms} is the phonon-generated microfield. Then, as for the absorption case,[6] we combine Eqs. (2) and (3), and since $\coth(\hbar\omega_{LO}/2kT)$ will be almost unity for ZnS at temperatures below about 100 °K, we obtain

$$E_p(T) = E_p(0) - S'[1 - \coth(\hbar\omega_{LO}/2kT)] , \qquad (4)$$

where $S' = \gamma'\beta$ and it is assumed that γ' does not change with temperature. To check the postulated dependence one can plot E_p at different temperatures vs $\coth(\hbar\omega_{LO}/2kT)$ and, if a straight line is obtained, compare its slope S' with predicted $\gamma'\beta$.

Experimental values of γ' were recently obtained[9,10] for ZnS(Cu,Cl) acceptor-to-band emission band. The temperature dependence of the position of the emission-band maximum for this transition was also found[10] to behave in a similar way to the edge-emission-band maximum of ZnS.

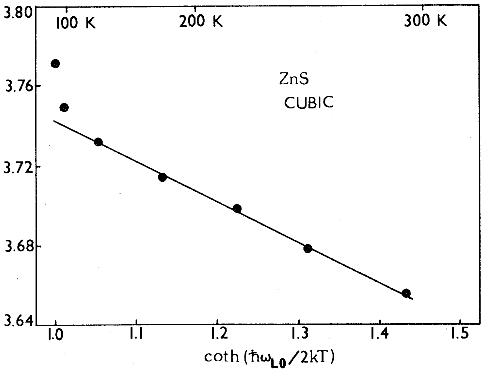

FIG. 1. Plot of the position of the edge-emission-band maximum E_p of ZnS vs $\coth(\hbar\omega_{LO}/2kT)$ where $\hbar\omega_{LO}$=43.5 meV.

It was also found previously that the effective phonon for this ZnS(Cu,Cl) emission corresponds to an LO phonon.[15] Thus, using the recent data[14] on the edge emission in ZnS, we plot E_p vs $\coth(\hbar\omega_{LO}/2kT)$. The straight line obtained in Fig. 1 for temperatures above 100 °K supports the postulated dependence. The slope of this plot will be the same in the case of ZnS(Cu,Cl) emission-band maximum, since, as was mentioned above, this acceptor-to-band transition behaves in a similar manner to the fundamental edge.[10] From Fig. 1 we obtain the slope $S' \simeq -0.20$ eV.

DISCUSSION

First, we will compare the value of the slope S' obtained from Fig. 1 with its expected value $\gamma'\beta$ from Eq. (4). The Franz-Keldysh coefficient γ' for the emission-band maximum of the acceptor-to-band transition was measured in ZnS(Cu,Cl) for both thin films[10] and crystals.[8,9] The value of $\gamma' \simeq -1.3\times10^{-12}$ eV cm^2/V^2, obtained for crystalline material,[9] will be used for the comparison, since γ' in thin films[10] (which is of the same order of magnitude) could be significantly affected by the surface potential and polarization effects present. In addition, it should be mentioned that, while for a crystal no temperature dependence of γ' was observed,[8,9] in films γ' was found to be temperature dependent.[10] Coefficient β [Eq. (2)] contains q_c, the polaron cutoff wave vector, the only parameter which cannot be chosen unambiguously. However, the requirement of a quasiuniform field along the tunneling distance demands that q_c satisfy the relation $q_c \leq \pi/a$. Judging from the straight line obtained from Fig. 1, we can conclude that β does not change (or changes insignificantly) with temperature, and can calculate q_c from $\beta = S'/\gamma'$. Thus, from values of $S' \simeq -0.20$ eV and $\gamma' \simeq -1.3\times10^{-12}$ eV cm^2/V^2, the value $q_c \simeq 1.45 \times 10^7$ cm^{-1} is obtained, satisfying the relation $\pi/2a \leq q_c \leq \pi/a$ for the quasiuniform field (for the exciton radius a see Table I).

For lower temperatures, below 100 °K, we expect that, as in the case of the absorption edge,[6] LA-phonon-generated piezoelectric fields will have a major influence on the temperature behavior of the edge emission with the dependence similar[6] to that described by Eq. (4).

It should also be mentioned that the Franz-Keldysh coefficient γ' of the emission-band maximum for this acceptor-to-band transition is very close to the value of the coefficient γ for the absorption edge.[16] Thus, we would expect similar behavior [Eq. (4)] in the case of the fundamental emission. Keeping this fact in mind, we can now make some estimates for CdS as well. The temperature dependence of the position of the emission-band maximum in CdS was found to follow the same $E_p \propto \coth(\hbar\omega_0/2kT)$ dependence[14]; and, similar to the case of the absorption in ZnS crystals,[6] it was also found[14] that different types of phonons were effective in different temperature ranges: The LA phonon was the effective one from 78 to 140 °K, while from 140 to 340 °K it was the LO phonon. The Franz-Keldysh shift of the emission band in CdS was also observed recently in the electric domain regions of the crystal.[11] Since it was possible to estimate only an approximate value for the electric field in the domain region,[11] no reliable value of γ' can be derived from these measurements. Nevertheless, from the results of the temperature dependence of the position of the edge-emission-band maximum,[14] one can obtain the slope $S' \simeq -0.15$ eV and compare this with β, using the data in Table I, for intermediate values of $q_c \leq \pi/a$. Thus the Franz-Keldysh coefficient $\gamma' \simeq -2.87 \times 10^{-12}$ eV cm^2/V^2 would correspond to $q_c = 3\pi/4a$, while $\gamma' \simeq -1.21 \times 10^{-12}$ eV cm^2/V^2 would correspond to $q_c = \pi/a$ (both values of γ' are for unpolarized light emission). These are to be compared with the Franz-Keldysh coefficient $\gamma \simeq -1.8 \times 10^{-12}$ eV cm^2/V^2 (for polarized light $\vec{E} \perp \vec{C}$) for the absorption edge.[17] The consistency with a similar comparison in ZnS is very good, considering the uncertainties in choosing q_c.

The strong piezoelectric fields due to LA phonons may also account for similar effects in III-V and II-VI semiconducting compounds.[6,13,18-21] However, in some cases the effect of phonon-generated fields might be more complicated than one-phonon cases described above for ZnS and CdS. In this context, for several different internal fields involved in the process, the combined effects of the fields should be considered.[22-24]

In summary, for the one-phonon case in ZnS and CdS, when different phonons are active in different temperature ranges,[6,14] the temperature dependence of the emission edge can be explained both qualitatively and quantitatively in the light of the internal Franz-Keldysh effect. Further studies on other materials, including measurements of the Franz-Keldysh effect as a function of temperature, which would clarify for each case both the $\Delta E \propto F^n$ dependence (n does not necessarily equal 2 for nonexponential edges) and the possible variations of γ and γ' with temperature, will be necessary before the model can be shown to provide a general applicability.

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