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EXCITON-ELECTRON SCATTERING IN HIGHLY EXCITED CdS SINGLE CRYSTAL*

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I. INTRODUCTION

Since the 1970s, the study of stimulated emission of CdS and other II—VI compound semiconductors has speeded up the development of the study of highly excited semiconductors. It was shown that the ex-el scattering induces the main recombination process that yields high gain above 100 K both experimentally and theoretically[1, 2]. The results obtained so far concern mainly the stimulated emission, and most of the efforts are devoted to the temperature dependence of emission spectra. Only a few works are concerning the dynamics of the luminescence due to scattering.

With the development of the study on the high-speed optical information processing, the optical nonlinearity and bistability in these II—VI compound materials become very attractive because of the short relaxation time of relevant processes and good response of excitons or other elementary excitations in these processes[3].

In this work, we have investigated the luminescence of ex-el scattering in highly excited CdS single crystal. From the temperature and excitation dependences of the emission peak, and from the picosecond study of the luminescence decay and the polarized luminescence of ex-el scattering due to A, B excitons, we have studied the static and dynamic behavior of luminescence induced by ex-el scattering.

II. EXPERIMENTAL RESULTS

The third harmonic of a mode-locked Nd : YAG laser (with the wavelength 355 nm, pulse duration 100 ps) is used to excite the CdS single crystal sample. The crystallographic axis c is parallel to the surface and perpendicular to laser beam. Fig. 1 shows the luminescence

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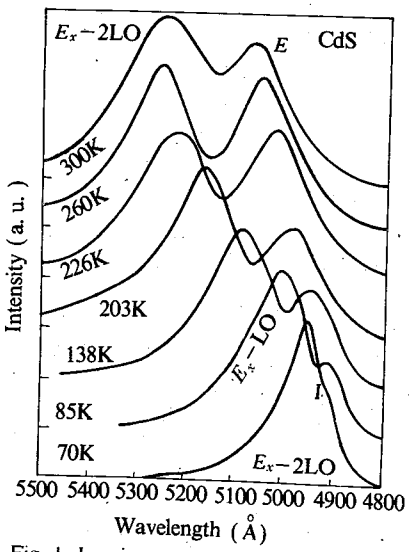

Fig. 1. Luminescence spectra of CdS smgle crystal at different temperatures, with the excitation intensity of 1 MW · cm^{-2}.

spectra of CdS single crystal at a temperature range from 70 K to 300 K, under the excitation of intensity 1 MW · cm^{-2}. When temperature is increased, the emission bands E_x-LO and I at 70 K evolve to a broad band E. E_x-LO is LO phonon replica of free exciton, I comes from the recombination of the exciton bounded on the neutral donor, and E is considered due to the emission of ex-el scattering. The peak positions of E and E_x-2LO shift to lower energy as the temperature is increased. The rate of change of the E band peak is $d\hbar\omega_e/dT \sim -6.5\times10^{-4}$ eV/K, and the rate of change of band gap is $dE_g/dT \sim -4.9\times10^{-4}$ eV/K. So the rate of change of E band is larger than that of band gap. It agrees with the former results of Refs. [2, 4].

Fig. 2 demonstrates that the luminescence bands E and E_x-2LO change with the excitation intensity I_{exc}. The luminescences of E and E_x-2LO increase when the excitation increases, but the latter increases much faster. It is also observed that the E band peak is red shifted when the excitation increases.

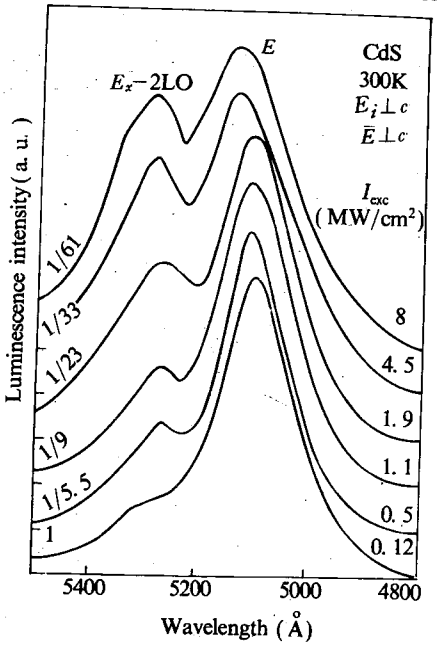

Fig. 2. The luminescence of CdS single crystal vs. excitation intensities at room temperature.

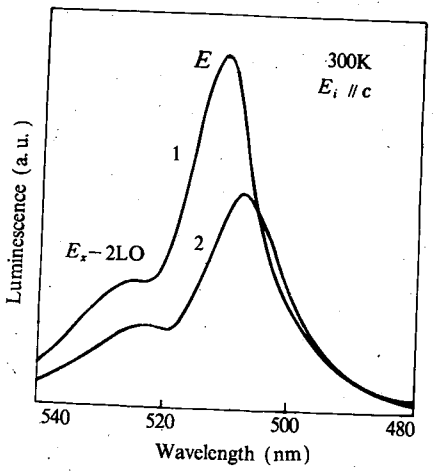

Fig. 3. The spectra of different polarized luminescences of CdS single crystal.
1, $E\perp c$; 2, $E//c$.

The luminescence spectra with polarizations $E\perp c$ and $E//c$ when the sample is excited by polarized light $E_i\perp c$ or $E_i//c$ are shown in Fig. 3. A red shift of the emission band peak

with polarization $E \perp c$, as compared with $E//c$, is obvious. Its value is 19 meV and is independent of the excitation intensity. This value is close to the splitting between the valence bands A and B.

III. Discussion

1. The concept of ex-el scattering was first introduced by Benoit a la Guilaume et al. to explain the recombination process in CdS crystal[1]. In the ex-el scattering process, the electron gains the energy and enters the higher energy states, while the exciton recombines and emits a photon of lower energy. The conservation of momentum and energy of the system are required in this process.

$$\boldsymbol{K}+\boldsymbol{k}_i=\boldsymbol{k}_f, \tag{1}$$

$$E_0+\hbar^2\boldsymbol{K}^2/2M+E_g+\hbar^2\boldsymbol{k}_i^2/2m_t=\hbar\omega+E_g+\hbar^2\boldsymbol{k}_f^2/2m_t \tag{2}$$

where $\boldsymbol{K}$ is the momentum of exciton; $\boldsymbol{k}_i$, $\boldsymbol{k}_t$ are the momentums of electron before and after scattering respectively; E is the energy of exciton in ground state where $K=0$; E_g is the band gap; and $\hbar\omega$ is the energy of emission photon. From Eqs. (1) and (2), one can obtain

$$\hbar\omega=E_0-E_K(M/m_e-1)-2\delta\sqrt{E_KE_{ki}M/m_e}, \tag{3}$$

where $0<\delta<1$, $E_K=\hbar^2K^2/2M$, $E_{ki}=\hbar^2k_i^2/2m_e$. Being a fermion, the electron will occupy the higher energy levels and the lower ones are occupied already when the excitation is increased, i. e. E_{ki} will increase and the emission photon energy will decrease as shown in Eq. (3). This is the reason for red shift of the emission with the increased excitation. According to Boltzmann's distribution law the kinetic energy of exciton and electron is $E\sim 3k_BT/2$. The emission photon energy is

$$\hbar\omega=E_g-3k_B(M/m_e-1+2\delta M/m_e)T/2-E_x^b, \tag{4}$$

which shows that the peak position is red-shifted when the temperature is increased, and this change is faster than the band gap. It accords with the experimental results qualitatively.

2. The dynamic equations of the ex-el scattering luminescence are

$$dn/dt=g_e-Anp, \tag{5}$$

$$dn_{ex}/dt=g_{ex}-n_{ex}/\tau-Bnn_{ex}, \tag{6}$$

where g_e, g_{ex} are the rates of the generation of electrons and excitons respectively; Anp is the recombination term of electron-hole pair; Bnn_{ex} corresponds to the radiative term of ex-el scattering interaction; n_{ex}/τ is the total (including radiative and nonradiative) recombination of excitons whose lifetime is τ. The stimulated emission threshold of the ex-el interaction is much lower than that of the exciton-exciton and exciton-MLO phonons scattering interaction at room temperature[2]. The experimental results show that the radiations corresponding to Anp

and n_{ex}/τ are much weaker than the luminescence of ex-el scattering. These processes are neglected in the discussion of ex-el process.

Suppose we stop the excitation at $t=0$, the densities of electron and exciton at this time are denoted by n^0 and n^0_{ex}, respectively. From the dynamic Eqs. (5) and (6), one obtains $n_{ex}=n^0_{ex}\exp(-Bn^0t)$. That means the luminescence of ex-el interaction decays according to single exponential law. The decay time $\tau_{ex-el}=1/Bn^0$ depends on the number of excited electrons in the conduction band. This decay time in picosecond time-domain is measured by a streak camera and is shown in Fig. 4.

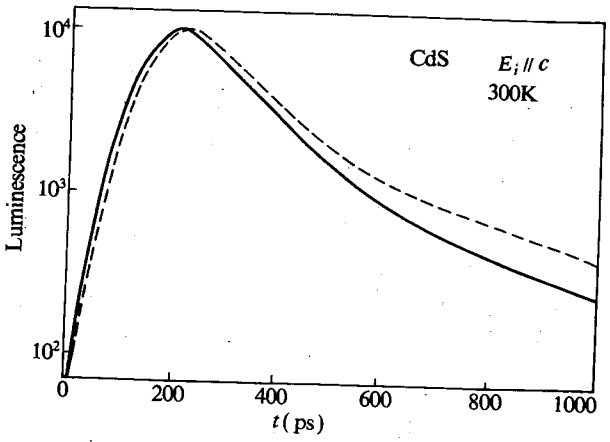

Fig. 4. The luminescence decay around 500 nm of CdS single crystal at room temperature.
——, $E\perp c$; ----, $E\parallel c$.

3. There are three valence bands Γ_9(A), Γ_7(B) and Γ_7(C) for the CdS single crystal of C_{6v} symmetry. The electric dipole transition between Γ_9(A) and Γ_7(conduction band) is allowed only for the $E\perp c$ polarized light. But that between Γ_7(B, C) and Γ_7(conduction band) is allowed for both the polarized $E\perp c$ and $E\parallel c$. The energy position of band peak shifts 19 MeV, and it equals the splitting of A, B bands. This indicates that the luminescences polarized for $E\perp c$ and $E\parallel c$ are corresponding to the ex-el scattering of A, B excitons with electron.

In case of excitation $E_i\parallel c$, only the B holes are generated. However, the luminescence related to A holes is observed, it can be interpreted as the result of relaxation of a part of B holes to A band. As shown in Fig. 4, when the crystal is excited by $E_i\parallel c$, $E\parallel c$ polarized luminescence reaches the maximum first and then decays quickly. The results are deconvoluted by a microcomputer. $\tau_A\sim 107$ ps and $\tau_B\sim 65$ ps are obtained. Let the hole relaxation time be τ_{B-A}, from

$$1/\tau_B=1/\tau_A+1/\tau_{B-A}, \tag{7}$$

$\tau_{B-A}\sim 166$ ps is obtained. This further confirms the holes relaxation from valence band B to A.

IV. Conclusion

1. The luminescence band of ex-el interaction is red-shifted with the increase of excitation.

2. Two kinds of excitons take part in the ex-el scattering process. They correspond to the excitons composed of electrons in the conduction band and the holes in B and A valence bands, respectively.

3. The luminescence from B exciton is of shorter wavelength than that of A exciton, and of a shorter decay time also.

4. There exists the hole relaxation from B valence band to A valence band.

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