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DYNAMICS OF LOCALIZED EXCITONS IN MIXED SEMICONDUCTING CRYSTALS

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II - EXPERIMENTAL

A cw mode-locked Ar+ laser and a synchronously pumped dye laser were used for excitation of samples. Luminescence from the (110) surface of Cd$_{x}$Zn$_{1-x}$Te crystal was collected by the backward scattering
geometry. The spectrum is analysed by double-monochromator equipped with a cooled photomultiplier. We employed a time-correlated single photon counting method for measuring decay behavior of emission intensities. The full widths at half maximum of the time response of the system were 425 ps and 350 ps for the pulse of the mode-locked Ar laser and that of the synchronously pumped dye laser, respectively. The time resolution of about 50 ps for decay times was obtained by using a convolution analysis.

III - RESULTS AND DISCUSSIONS

III.1 Dynamics of localized excitons under band-to-band excitation

Figure 1 shows time-integrated emission spectra of Cd$_{x}$Zn$_{1-x}$Te crystals ($x=0.32$) observed at various temperatures under band-to-band excitation at 514.5 nm with an average power of 0.5 mW. At lower temperatures we see two emission bands (X band and LE band) below the band gap (E$_g$ = 16930 cm$^{-1}$). When the temperature is raised, intensity of LE band decreases more rapidly than that of X band and X band becomes dominant above 21K.

The decay kinetics of the luminescence bands was measured; decay times depend on the energy at which we monitor. In Fig. 2 are illustrated decay curves measured at 16790 cm$^{-1}$ for temperatures

![Graph](image-url)

**Fig. 1** - Emission spectra at various temperatures with excitation at 514.5 nm.

![Graph](image-url)

**Fig. 2** - Decay curves of emission intensities measured at 16790 cm$^{-1}$ for various temperatures. Temperatures, (a) 21 K, (b) 17 K, (c) 12 K, (d) 6.6 K, (e) a time response of the laser pulse.
between 6.6K and 21K. It is clear that these decay curves are not exactly exponential. In order to obtain decay times, we calculated decay kinetics by convoluting exponential functions with instrumental response. Assuming that a decay curve consists of three components: a fast decay component without a rise time, a fast decay component with a finite rise time and a slow component, we used the following kinetic function:

\[ f(t) = a_1 \exp(-t/\tau_f) + a_2 (\exp(-t/\tau_r) - \exp(-t/\tau_f)) + a_3 \exp(-t/\tau_s), \]

where \( \tau_f, \tau_r, \tau_s, a_1, a_2, a_3 \) are introduced as adjustable parameters. The convoluted curves giving the best fits to the experimental ones are shown in Fig. 2 by open circles. Above 21K, we can get best fits by taking \( \tau_f = 0 \). The fast components are dominant and the decay time, \( \tau_f \), decreases with increase of temperatures. From the argument of rate equations, we find that the fast component without a rise time corresponds to the decay of excitons which are initially distributed in the tail state by the exciting pulse. The fast component with a rise time is due to excitons transferred between random potential wells and the rise time corresponds to the average time of transfer.

From the temperature dependence of \( \tau_f \), we can obtain activation energies of excitons. The Arrhenius plot gives us two kinds of activation energies, \( E_{a1} \) and \( E_{a2} \). In Fig. 3 are summarized \( E_{a1} \) and \( E_{a2} \) as a function of exciton energies. Smaller activation energy, \( E_{a1} \) (open circles) decreases linearly with exciton energy intercepting the \( E = 0 \) axis at \( \omega = 16830 \text{ cm}^{-1} \). Larger one (crosses) is independent of exciton energy and its value is in good agreement with the binding energy of free excitons in \( \text{Cd}_x\text{Zn}_{1-x}\text{Te} \). Below \( \omega_e \), excitons have an activation energy depending on the energy, whereas excitons above \( \omega_e \) have no activation energy within our experimental errors, indicating that they are delocalized. We note that the activation energy of the exciton at the energy \( \omega \) coincides well with the energy difference between \( \omega_e \) and the luminescence energy \( \omega \) of this exciton. Thus, exciton states below \( \omega_e \) are effectively localized and their activation energies correspond to the localization energies from \( \omega_e \). When the temperature is raised, these localized excitons are thermally activated into the hopping states above \( \omega_e \). We conclude that there exists "an effective edge" of exciton transfer above which excitons are mobile and have a high transfer rate into the tail state.

### III.2 Transformation of RRS into luminescence in a second order optical process

In Fig. 4 are illustrated time-integrated spectra of secondary emission measured by resonant excitation below the band gap. Sharp lines of the secondary emission are observed and the shift of their peak positions correlates with the excitation energy, \( \omega_e \). The energy shifts of \( \text{LO}_1 \) and \( \text{LO}_2 \) lines from \( \omega_e \) are close to the LO phonon
energies of pure CdTe and ZnTe crystals, respectively /5,6/. When $\omega_i \leq 16702$ cm$^{-1}$, TO$_2$ line is observed whose energy shift corresponds to the TO phonon energy of pure ZnTe crystals. The full width at half maximum of these lines is about 8 cm$^{-1}$ being independent of $\omega_i$, whereas that of the laser line is about 7 cm$^{-1}$. Intensities of these lines increase when $\omega_i$ approaches the peak energy of LE band.

In fig. 5 is represented decay behavior of the secondary emission intensity monitored at the peak position of LO$_2$ lines for various $\omega_i$'s. It is clear that the decay curve for $\omega_i = 16790$ cm$^{-1}$ exhibits a single exponential decay with a time constant of 0.85 ns. A time response of RS is expected to be as short as the duration of the excitation pulse. Therefore, the long decay shown in fig. 5(a) leads us to conclude that LO$_2$ line for $\omega_i = 16790$ cm$^{-1}$ is not due to RS but due to resonance luminescence with emission of LO phonons.

By decreasing $\omega_i$, as shown in fig. 5(b)-(d), a short-lived component appears in addition to the long-lived component in the decay curve. The short-lived component seems to follow the temporal profile.
of the laser pulse. Assuming that decay curves can be fitted by a sum of two exponential functions (three exponential functions for \( \omega_1 = 16681 \) and 16621 cm\(^{-1}\)), we have determined decay times of short-lived component, \( \tau_s \), and long-lived component, \( \tau_L \), from the convolution analysis. The best fit of the short-lived components could be obtained with values of \( \tau_s \) less than 50 ps. Since the time response of the short-lived component is as short as that of the laser pulse, this component can be attributed to RS.

The long-lived components, however, exhibit an exponential decay and their decay times depend on \( \omega_1 \). The values of \( \tau_L \) coincide well with the lifetimes of the localized excitons at the energy \( \omega_1 \), which were determined under band-to-band excitation. Therefore, the long-lived component of the LO lines is attributed to the LO phonon-assisted luminescence of the localized excitons that are selectively excited as a real state at the energy \( \omega_1 \).

The emission spectra in fig. 4 can be characterized as follows: for \( \omega_1 \leq 16747 \) cm\(^{-1}\), both luminescence and RS processes contribute to the "Raman-like" lines in the secondary emission spectra. When \( \omega_1 \) is tuned on to the luminescence peak of localized excitons, second order optical process is transformed into the luminescence process keeping the spectral shape unchanged.

The continuous transition of RRS into luminescence in the mixed semiconducting crystal can be compared to the experiment on iodine molecules /7/. The continuous transition has been also observed in I\(_2\) but the intensity ratio of luminescence to RS becomes constant at large values of off-resonance energy. This result has been interpreted by the theory /8/ in the motional narrowing limit. In our case, however, the intensity ratio continues to decrease when off-resonance energy is increased. Therefore, this theory cannot account for our result in the off-resonance region; this suggests that the non-motional narrowing effect as was pointed out by Aihara /9/ is seen in the second order optical process in the mixed semiconducting crystal.

IV. SUMMARY

We have measured the time response of the secondary emission in Cd\(_{0.5}\)Zn\(_{0.5}\)Te crystals in sub-nanosecond time region by band-to-band excitation and resonant excitation. From the temperature dependence and the energy dependence of exciton dynamics, we have found the effective edge of energy transfer in the tail state of excitons. Excitons below the edge are effectively localized, whereas above the edge they are delocalized. The temporal behavior of the emission intensity under resonant excitation allowed us to find, for the first time, the continuous transition from RRS to resonant luminescence in the mixed semiconducting crystal as a function of incident energies.

REFERENCES