

Subnanosecond spectroscopy of disorder-localized excitons in $\text{CdS}_{0.53}\text{Se}_{0.47}$

J. A. Kash and Arza Ron*

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

E. Cohen*

Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 24 June 1983)

Time-resolved luminescence spectra from excitons in $\text{CdS}_{0.53}\text{Se}_{0.47}$ at 2 K with 250 psec resolution reveal line narrowing at short times, followed by broadening and a shift towards lower energy, during the first few nanoseconds. We interpret the spectral diffusion as exciton transfer between states localized as a result of random potential fluctuations of the mixed crystal. The variation of luminescence decay kinetics with temperature suggests that a gradual transition from localized to extended states exists within a disorder-broadened exciton band.

Intrinsic exciton spectra in semiconductor alloys are broadened because of the random potential fluctuations which arise from local compositional fluctuations.¹⁻⁵ Recently, the problem of exciton dynamics within the inhomogeneously broadened band has been studied in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (Ref. 6) and in $\text{CdS}_x\text{Se}_{1-x}$.^{7,8} In the latter case, phonon-assisted exciton transfer between localized states within the alloy-broadened exciton band has been proposed⁸ to explain the spectral diffusion of selectively excited excitons. Previously observed cw spectra reflect the steady-state distribution of excitons as determined by the exciton transfer and the exciton lifetime (which at low temperatures is mainly radiative).

In order to follow the evolution of exciton diffusion, time-resolved spectra are required. While for indirect band-gap materials such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x > 0.44$) nanosecond resolution suffices,⁶ subnanosecond resolution is required for direct band-gap materials such as $\text{CdS}_x\text{Se}_{1-x}$. Such a technique has previously been employed⁹ in the study of bound-exciton dynamics in $\text{GaAs}_{1-x}\text{P}_x$ doped with nitrogen.

In this work we report the results of a study of time-resolved spectroscopy of $\text{CdS}_{0.53}\text{Se}_{0.47}$ in the temperature range 2–45 K. The results confirm the model of exciton transfer between localized states and reveal thermally activated processes into higher-energy localized and extended exciton states. The extended exciton states dominate the dynamics at elevated temperatures (> 40 K).

Time-resolved spectra were obtained by selective excitation of $\text{CdS}_{0.53}\text{Se}_{0.47}$ single crystals with a picosecond dye laser. The laser pulse width was 10 psec with 1 nJ pulse energy; the repetition rate was 70 MHz. This corresponds to 3×10^9 photons per pulse, and an excited carrier concentration of roughly 10^{16} cm^{-3} . The luminescence decay dynamics were measured with 250-psec resolution by a time-correlated photon counting system described elsewhere.¹⁰ Time-resolved spectra (with the same time resolution) were obtained by reconstruction from a series of decay kinetics taken at closely spaced photon energies.

Figure 1 shows the time-integrated luminescence spectrum for above band-gap excitation. As previously noted^{7,8} for this exciton band, the luminescence peak is at lower energy than the center of the reflectance-spectrum structure, which we will refer to as the reflectivity peak. The

reflectivity-peak position is indicated in Fig. 1. Also shown in Fig. 1 is the $T = 2$ K effective lifetime (defined below).

Figure 2 shows three sets of time-resolved spectra taken at the indicated delays after the exciting pulse. Figure 2(a) is for above-band-gap excitation. Figures 2(b) and 2(c) are for laser excitation energies E_{exc} within the exciton band as indicated. When selective excitation within the exciton band is used (as opposed to above band-gap excitation), it is desirable to monitor the luminescence from excitons resonantly created by the laser. Because of scattered light, the luminescence cannot be measured directly at the excitation energy. However, the luminescence in the LO_1 phonon replica was found to faithfully reproduce that of the main peak whenever direct comparison was possible. Thus the luminescence in Figs. 2(b) and 2(c) is monitored in the LO_1 replica. Note that the energy axis in Figs. 2(b) and 2(c) has been shifted by the 25.5-meV phonon energy so as to correspond to the actual exciton energy.

Figure 3 shows the variation in decay kinetics with temperature at two exciton energies (above band-gap excitation). The kinetics, monitored over three to four decades, were typically nonexponential, especially at low temperatures. However, in order to display their dependence on

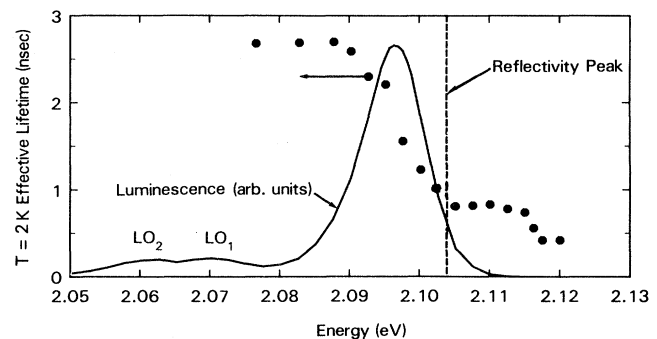


FIG. 1. (Solid line) Time-integrated exciton luminescence at $T = 2$ K. The LO_1 and LO_2 phonon sidebands are indicated. (Points) $T = 2$ K effective lifetime τ^* vs exciton energy. The lowest-energy ($E < 2.085$ eV) lifetimes are measured with selective excitation to avoid interference from the phonon sidebands. Also indicated is the reflectivity peak.

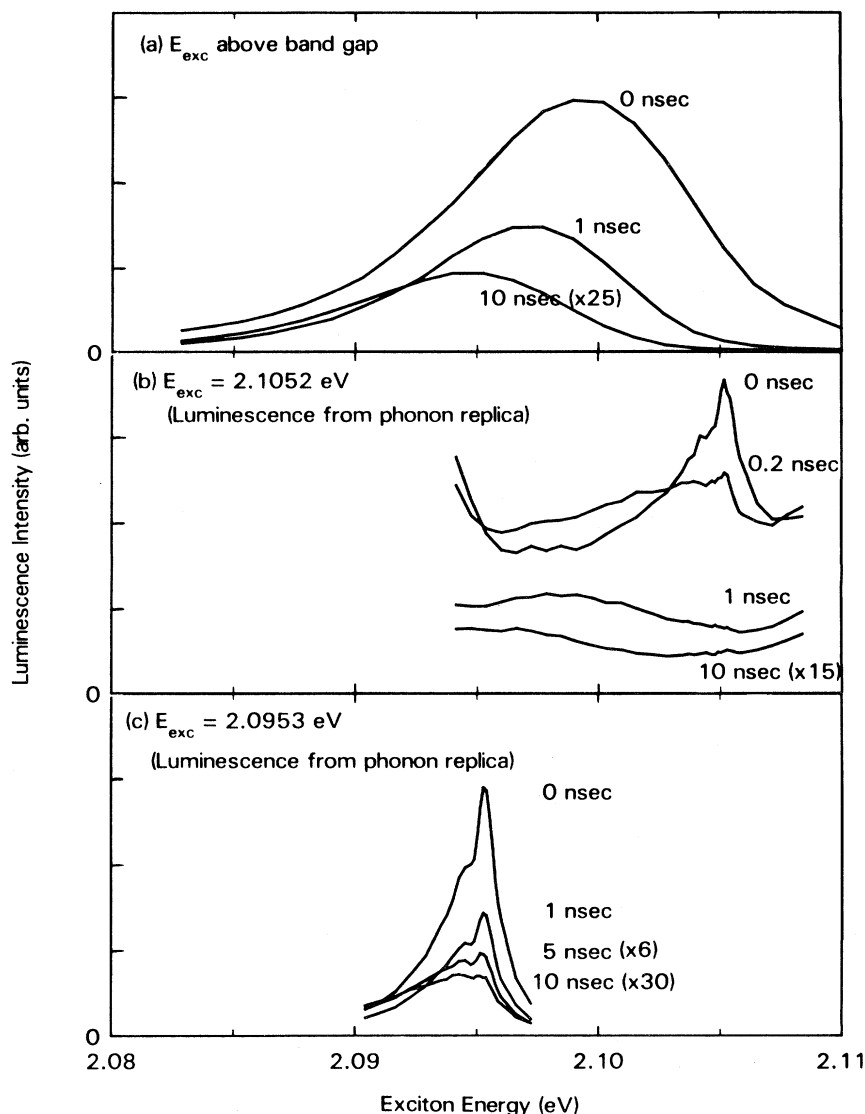


FIG. 2. Time-resolved spectra for the indicated excitation energies E_{exc} . As explained in the text, the luminescence in (b) and (c) is monitored in the LO_1 phonon replica and the energy scale is shifted by the 25.5-meV phonon energy.

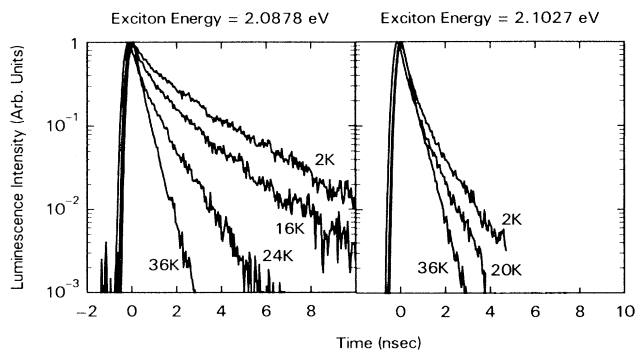


FIG. 3. Exciton decay kinetics at various temperatures for two different exciton energies. Excitation is above the band gap.

citon energy or on temperature, an “effective lifetime” τ^* was defined as the average slope of $\ln(I)$ in the second decade of the kinetics (10^{-1} – 10^{-2} in Fig. 3). Different criteria for τ^* produced slightly different values, but the qualitative trend in the lifetime shown in Fig. 1 remained unchanged.

We first argue that the observed luminescence is due to radiative recombination of intrinsic (rather than impurity-bound) excitons. As indicated in Fig. 1 the exciton luminescence peak is at lower energy than the reflectance peak. As $x \rightarrow 1$ in CdS_xSe_{1-x} , this splitting decreases smoothly⁷ and the luminescence band approaches that of the polariton in CdS. The low-temperature kinetics also suggest that the band is intrinsic. As can be seen in Fig. 1, a lower limit for the exciton radiative lifetime is 2.7 nsec, taken as that corresponding to excitons deep in the band. Wiesner and Heim¹¹ measured polariton lifetimes in pure

CdS and found them to range between 0.3 and 2.5 nsec. The lifetime of 2.5 nsec corresponds to bottleneck polaritons and is thus a lower limit on the radiative lifetime. On the other hand, measured lifetimes of excitons bound to neutral donors or acceptors in CdS are shorter, as measured by Henry and Nassau¹² to be 1.0 and 0.5 nsec, respectively. We thus conclude that the observed emission in CdS_{0.53}Se_{0.47} is due to intrinsic excitons.

In Ref. 8 a model was developed which explained the line shape of selectively cw excited spectra in terms of exciton transfer between localized states set up by the random potential fluctuations. According to this model, an exciton localized at a site with energy E_a can migrate onto another site having energy E_b . The energy difference $E_a - E_b$ is taken up by acoustic phonons. At low temperatures ($kT \ll E_a - E_b$), excitons can either decay radiatively or migrate onto sites of lower energy. Consequently, the decay curves can be expected to be nonexponential and the time-resolved spectra will shift towards lower energies as time elapses. The overall decrease in luminescence intensity is due to the radiative recombination process. The shift in the time-resolved spectra reflects the varying distribution of excitons in the band during their lifetime. This is experimentally observed, as shown in Fig. 2. The spectral shift with time is more pronounced for excitation at the higher-energy part of the exciton band [compare Fig. 2(b) with Fig. 2(c)], which can be explained by a combination of two related facts: First, the density of states $g(E)$ in the exciton band tail decreases with decreasing exciton energy E , resulting in fewer available sites for tunneling. Second, because $g(E)$ is smaller, the average separation between sites with localized states increases with decreasing exciton energy. This results in a smaller overlap integral, and hence a smaller tunneling probability per available site. The shorter τ^* at higher exciton energy seen in Fig. 1 is a result of faster exciton migration into lower-lying states.

In Fig. 2(c), which is representative of all spectra with $2.077 \text{ eV} < E_{\text{exc}} < 2.095 \text{ eV}$, the time-resolved spectral shape is nearly constant and the luminescence decay nearly exponential. [There is still a small change in spectral shape in Fig. 2(c); the change is even smaller for lower E_{exc} .] Thus, as suggested by Permogorov *et al.*,⁷ exciton transfer in this region is negligible. The observed line shape is due to a strong acoustic phonon sideband.¹³ In conformance with this interpretation, this same spectral shape is seen at $t=0$ (i.e., prior to exciton transfer) in Fig. 2(b). If, as suggested in Ref. 8, the shoulder resulted from residual exciton transfer then it should not exist at $t=0$. Finally, we note that at the lowest excitation energies studied ($E_{\text{exc}} < 2.070 \text{ eV}$), the spectral shape is narrow, with no shoulder. Here, however, the kinetics are too rapid to be resolved. For these excitation energies, the emission is no longer luminescence, but instead is Raman scattering.

As the temperature is increased above $\sim 15 \text{ K}$, the luminescence decay rate increases, as seen in Fig. 3. We find that τ^* can be well fitted to the expression

$$[\tau^*(E, T)]^{-1} = [\tau_0^*(E)]^{-1} + B(E) \exp[-E_a(E)/kT]$$

over the range $T = 15$ to 40 K . Here τ_0^* and B depend only on the exciton energy E . τ_0^* is the $T = 2 \text{ K}$ effective lifetime as shown in Fig. 1(b). $E_a(E)$ is an activation energy. Its dependence on exciton energy is shown in Fig. 4, along with

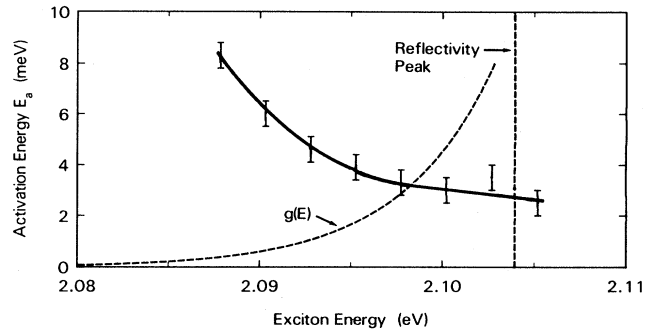


FIG. 4. Activation energy vs exciton energy. A smooth curve is drawn through the data. Also shown is the approximate density of states $g(E)$ (after Ref. 8) and the position of the reflectivity peak.

an approximate, exponential^{2,8} density of states $g(E)$.

Two additional experimental observations should be mentioned. Above 40 K , the decay curves throughout the entire exciton band are identical, being exponential over four decades with a lifetime of 0.42 nsec . Also, for exciton energies above about $2.115 \pm 0.002 \text{ eV}$ (the exact energy is hard to ascertain), the decay curves do not vary with temperature in the range $2\text{--}45 \text{ K}$.

We explain these observations in terms of thermal activation of the excitons into higher-energy localized and extended states, which have a large density of states. The activation energies of excitons deep in the band indicate that as temperature increases they transfer into higher-lying localized states near $E \sim 2.105 \text{ eV}$, and not directly into extended states. For exciton energies in the range $2.105\text{--}2.115 \text{ eV}$, the decay curves still vary with temperature, but due to the accuracy of our thermometer and uncertainty in deducing τ_0^* we could not determine an activation energy. However, the existence of a temperature dependence indicates that at least some of the states in this interval are still localized. We cannot determine in these experiments the existence of a sharp mobility edge. For $T > 40 \text{ K}$, excitons are fully activated into extended states, resulting in uniform, exponential decay curves throughout the band. The short lifetime (0.42 nsec) is presumably determined by non-radiative recombination, as extended excitons have a greater probability to reach deep traps.

Finally, we have noted that changes are observed in the kinetics as a function of laser intensity. Small changes are also observed at different laser repetition rates. We ascribe these changes to saturation of deep traps (with lifetime between $\sim 1 \mu\text{sec}$ and 20 nsec judging from the repetition rate dependence). The data reported here are for a repetition rate of 70 MHz ; at a rate of 700 kHz effective lifetimes decrease about 10% while derived activation energies increase about 40% . These changes do not alter our interpretation of the data.

In conclusion, time-resolved spectroscopy demonstrates that exciton transfer takes place throughout the disorder localized exciton band. The temperature dependence of decay kinetics reveals the importance of higher-energy extended states at elevated temperatures, and yields indirect evidence for a transition (possibly gradual) from localized to extended exciton states. These phenomena are likely to be observed in many semiconductor alloys.

ACKNOWLEDGMENTS

We thank Dr. M. D. Sturge for his helpful comments. This work was supported in part by the U.S. Navy Office of Naval Research under Contract No. N00014-80-C-0376.

*On sabbatical leave from the Solid State Institute, Technion, Israel Institute of Technology, Haifa 32000, Israel.

¹R. J. Nelson, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), p. 319.

²S. D. Baranovskii and A. L. Efros, *Fiz. Tekh. Poluprovodn.* 12, 2233 (1978) [*Sov. Phys. Semicond.* 12, 1328 (1978)].

³L. G. Suslina, A. G. Plyukhin, D. L. Federov, and A. G. Areshkin, *Fiz. Tekh. Poluprovodn.* 12, 2238 (1978) [*Sov. Phys. Semicond.* 12, 1331 (1978)].

⁴O. Goede, L. John, and D. Hennig, *Phys. Status Solidi (b)* 96, 671 (1979).

⁵Shui Lai and M. V. Klein, *Phys. Rev. Lett.* 44, 1087 (1980).

⁶M. D. Sturge, E. Cohen, and R. A. Logan, *Phys. Rev. B* 27, 2362 (1983).

⁷S. Permogorov, A. Reznitskii, S. Verbin, G. O. Müller, P. Flögel, and M. Nikiforov, *Phys. Status Solidi (b)* 113, 589 (1982).

⁸E. Cohen and M. D. Sturge, *Phys. Rev. B* 25, 3828 (1982).

⁹J. H. Collet, J. A. Kash, D. J. Wolford, and J. Thompson, *J. Phys. C* 16, 1283 (1983).

¹⁰J. A. Kash, J. H. Collet, D. J. Wolford, and J. Thompson, *Phys. Rev. B* 27, 2294 (1983).

¹¹P. Wiesner and U. Heim, *Phys. Rev. B* 11, 3071 (1975).

¹²C. H. Henry and K. Nassau, *Phys. Rev. B* 1, 1628 (1970).

¹³This wing, which results from a convolution of phonon-assisted absorption and phonon-assisted emission, is similar to that seen for the bound I_1 exciton in CdS, as in Ref. 12.