Time-resolved photoluminescence of excitons in $CuInS_2$ crystals

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Contents

Introduction

$CuInS_2$ ternary semiconductor

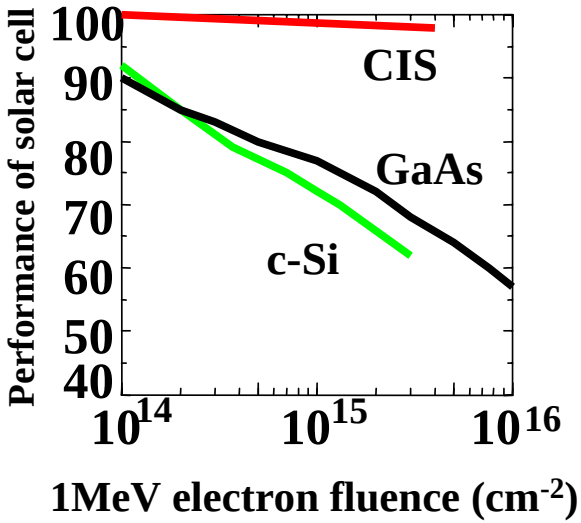
promising material for thin-film solar cell

advantage bandgap of 1.5 eV

large absorption coefficient

non-toxic material

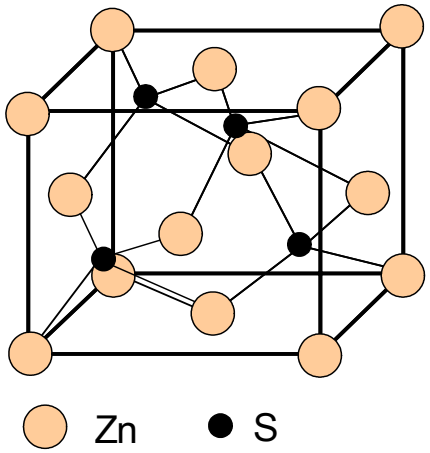
excellent resistivity for cosmic radiations



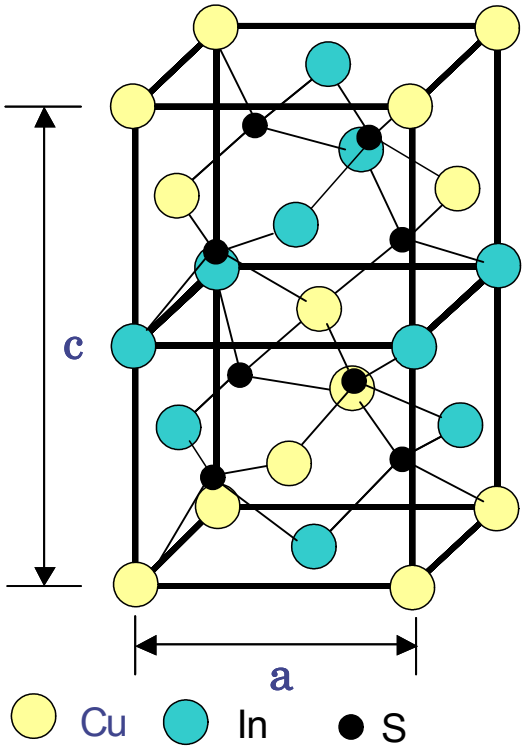
the highest conversion efficiency 12.5%

For further improvement of the efficiency it is important to clearly understand its fundamental properties.

Crystal structure of $CuInS_2$

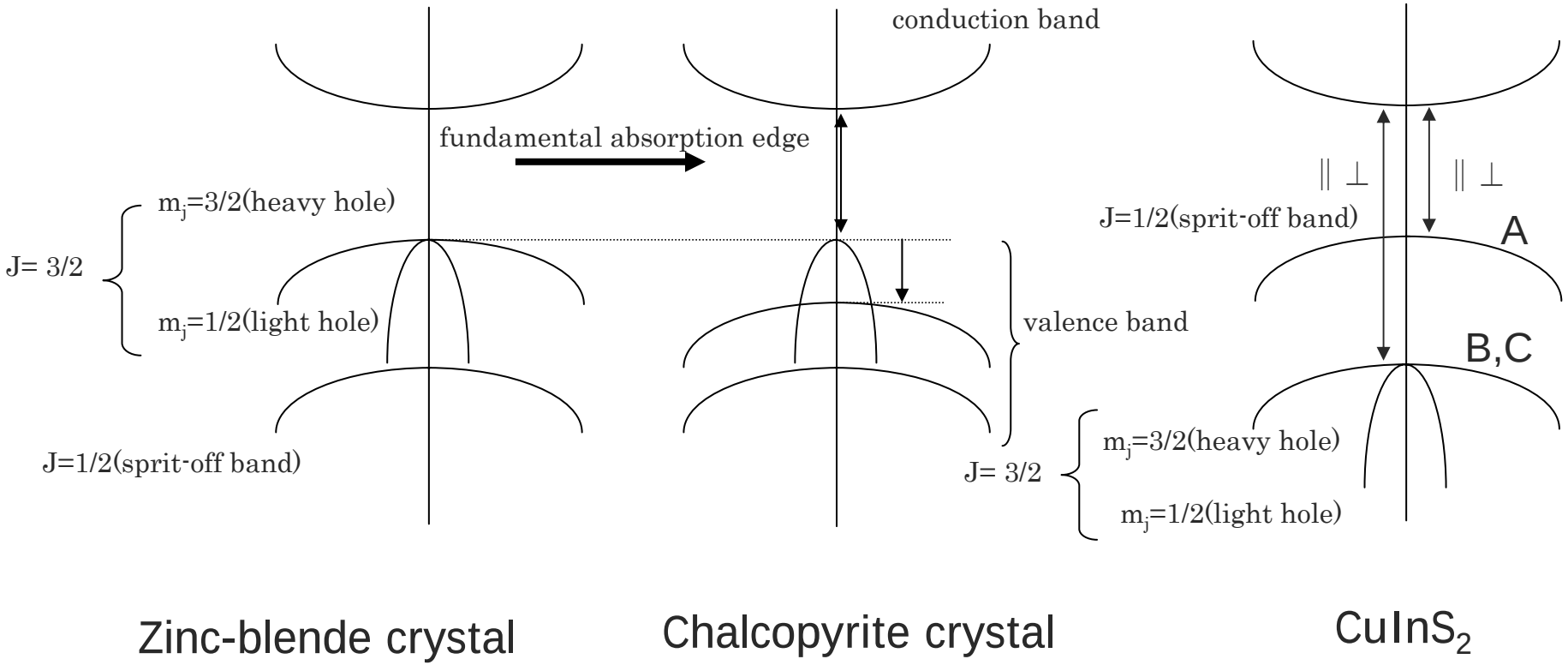


Zinc-blende structure



Chalcopyrite structure

Band structure in the band gap region

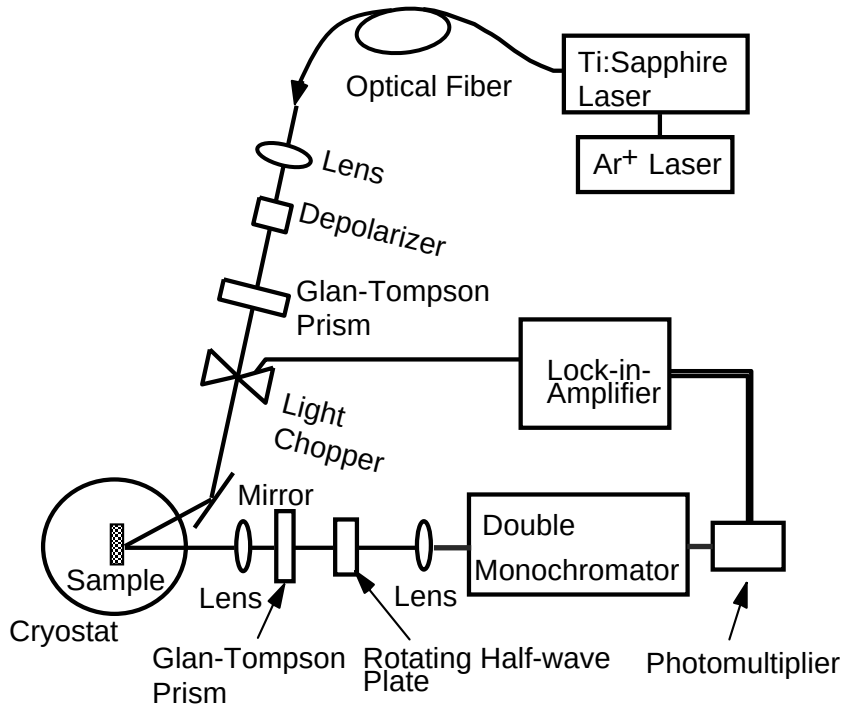


2. Relaxation of excited carriers

- Photoluminescence excitation (PLE) spectra is useful for examining
  - correlations between excitation states and PL states
  - relaxation and recombination processes.

- In this work,
  - detailed PLE spectra have been obtained using tunable leaser.
  - The spectra have sharp and interesting peaks and dips. Some of them are associated with excitons.
  - The relaxation model is presented.
  - The probability of radiative recombition is investigated by photoacoustic spectra.

Measurement system of PL and PLE spectra



Ti:sapphire laser

wavelength 735～840nm (1.48～1.69eV)

Measurement conditions

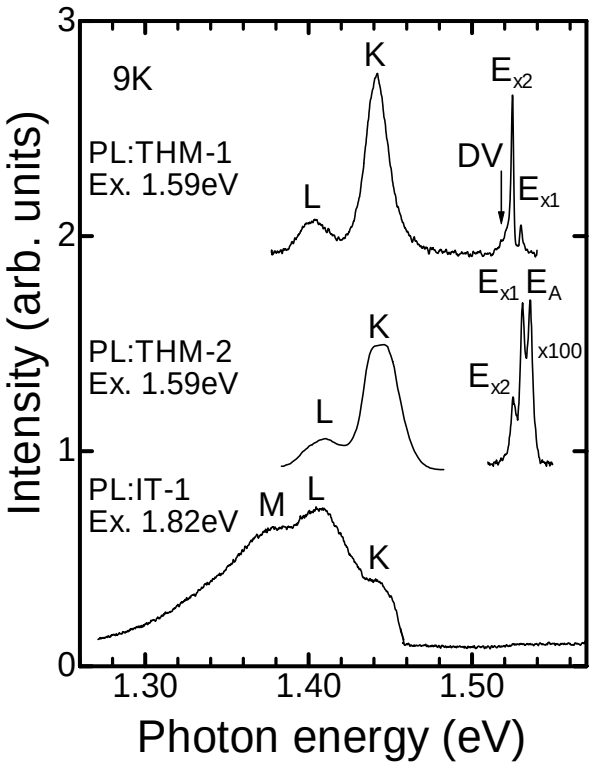
wavelength 735～840nm (1.48～1.69eV)

spot area ϕ 1mm

excitation power density 0.4 W/cm^2

temperature 10～60K

Photoluminescence (PL) spectra



Emission line	Photon energy (eV)	Assignment[3-5]
E_A	1.535	"*A*" free exciton
E_{x1}	1.530	Bound exciton
E_{x2}	1.525	Bound exciton
DV	1.52	Donor to valence band transition
K	1.44	Donor-acceptor pair transition
L	1.41	Donor-acceptor pair transition
M	1.38	Donor-acceptor pair transition

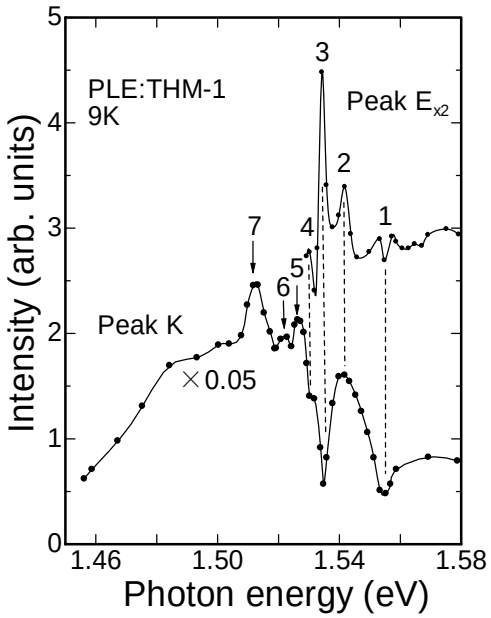
References

3. J. J. M. Binsma, L. J. Giling and J. Bloem, J. Lumin. **27** 55 (1982).
4. H. Y. Ueng and H. L. Hwang, J. Phys. Chem. Solids **50** 1297 (1989).
5. K. Wakita, H. Hirooka, S. Yasuda, F. Fujita, and N. Yamamoto, J. Appl. Phys. **83** 443 (1998).

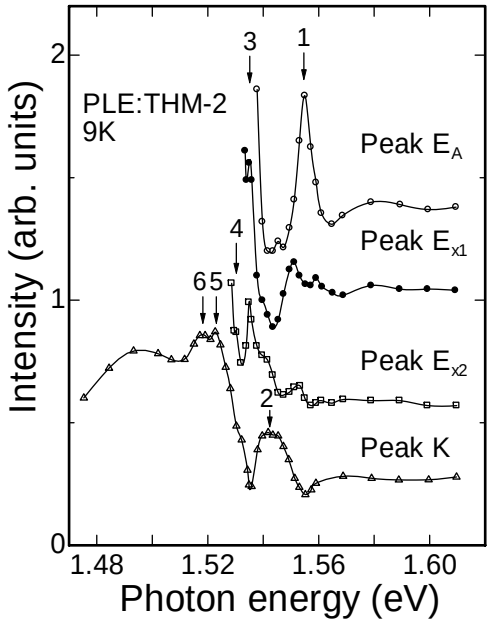
Photoluminescence excitation (PLE) spectra

Number	Photon energy (eV)	Corresponding transition	
1	1.555	"*B*" and "*C*" free exciton	($E_{B,C}$)
2	1.542	unknown	
3	1.535	"*A*" free exciton	(E_A)
4	1.530	Bound exciton	(E_{x1})
5	1.525	Bound exciton	(E_{x2})
6	1.521	Donor to valence band transition	(DV)
7	1.512	unknown	

THM-1



THM-2



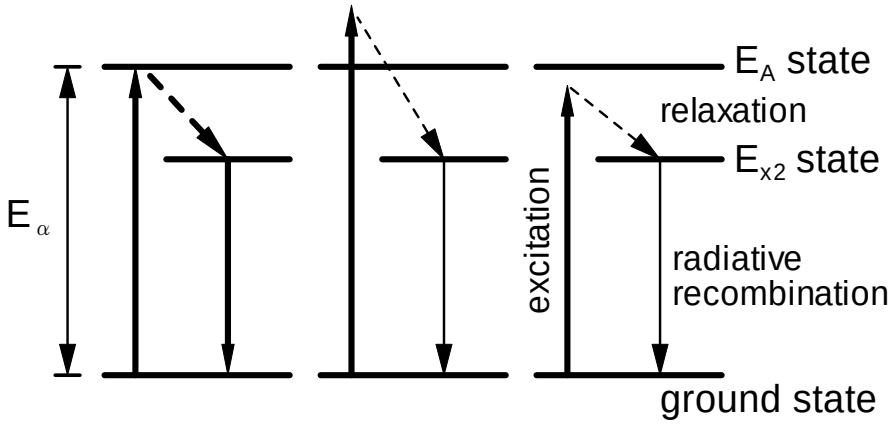
Relaxation model

The relationship between the emission intensity I_{em} and the excitation intensity I_{ex} is given by

$I_{em} = P_{abs} P_{rel} P_{em} I_{ex}$,

where P_{abs}, P_{rel}, and P_{em} are the absorption probability of an incident photon in the crystal, the relaxation probability of the excited electron-hole pairs to the radiative recombination state, and the radiative recombination probability after relaxation, respectively.

The relaxation probability is therefore the key factor that determines whether a peak or dip appears at the same energy in the PLE spectra.

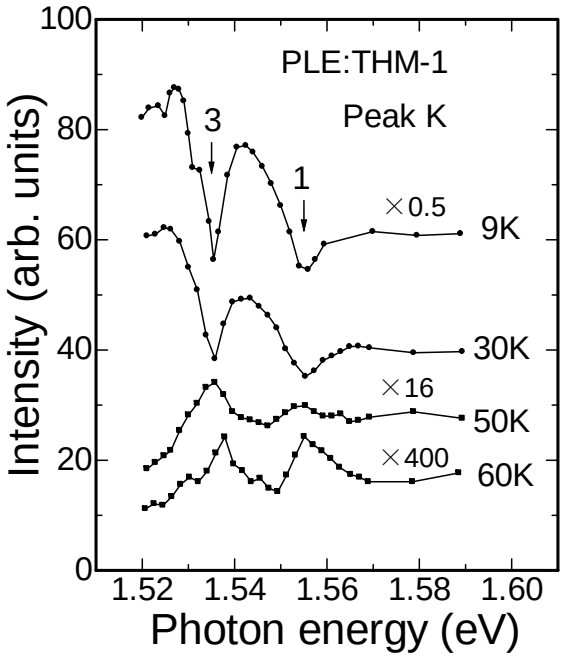


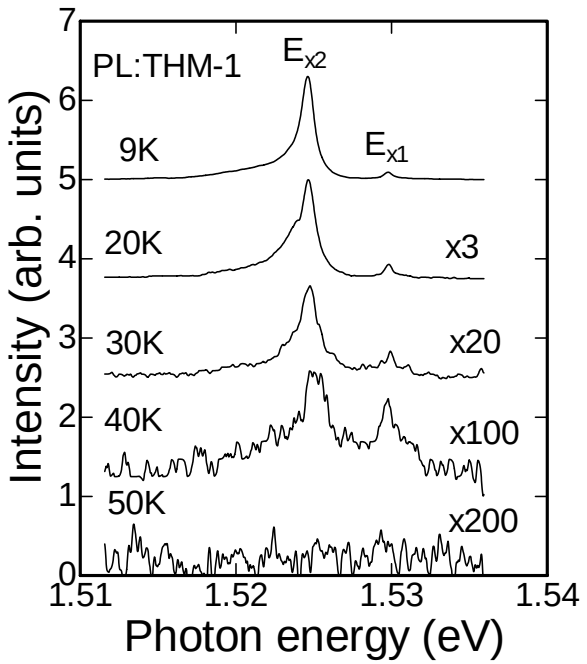
(a) $E_{EX} = E_{\alpha}$ (b) $E_{EX} > E_{\alpha}$ (c) $E_{EX} < E_{\alpha}$

The electron-hole pairs excited with energy E_{α} must effectively relax to the E_{x2} state (a) compared with excitation energy other than E_{α} (b) and (c).

The reason why the electron-hole pairs excited with energy E_{α} effectively relax to the E_{x2} state is that such excitation efficiently generates "*A*" free excitons.

Temperature dependence of PLE and PL spectra



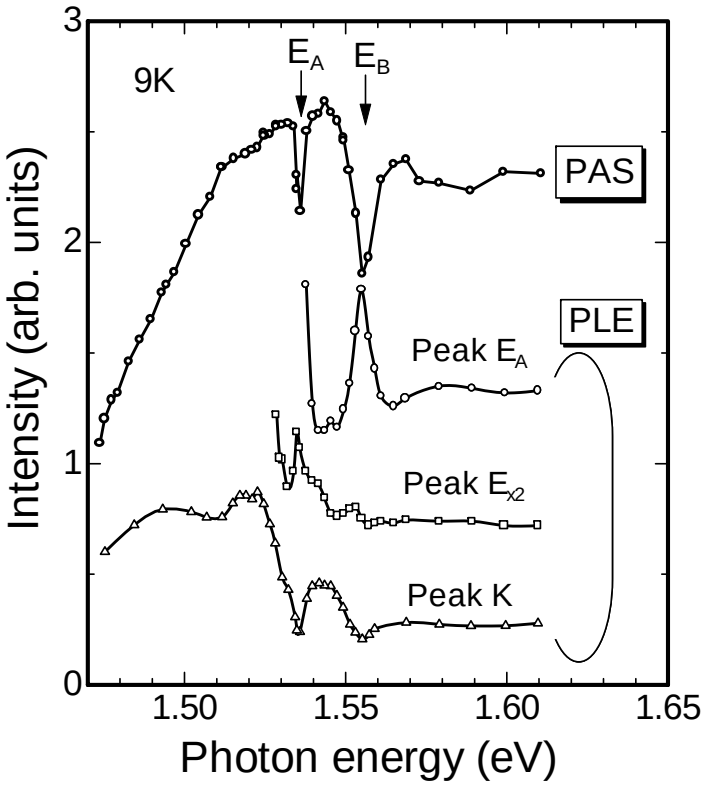


The temperature at which the dips in the PLE spectra change into peaks coincides with the quenching temperature of the bound exciton emissions.

Above 50 K, however, the pairs do not relax to bound excitons, instead relaxing to states of donor-acceptor pair emission because the bound exciton emissions of E_{x1} and E_{x2} are quenched. The PLE spectra therefore, exhibit peaks at $E_{B,C}$ and E_A due to relaxation to states of donor-acceptor pair emission.

Photoacoustic (PA) Spectra

PA and PLE spectra



To confirm our assumption that under resonant excitation at free exciton energies probability of radiative recombination increase, we investigated nonradiative recombination measuring photoacoustic (PA) spectra.

For our PA spectrum, dips at the E_A and E_B energy indicates an increase in the radiative recombination probability compared to that beside the dip, resulting in the high generation efficiency of "A" and "B" free excitons, respectively.

Conclusions (1)

- PLE spectra of single crystals of $CuInS_2$ were investigated.
- PLE spectra exhibited many peaks and dips near band edge.
- We proposed a relaxation process to account for the features detailed in the PLE spectra.
- The probability of radiative recombination under resonant excitation at exciton energy was verified by photoacustic spectra.

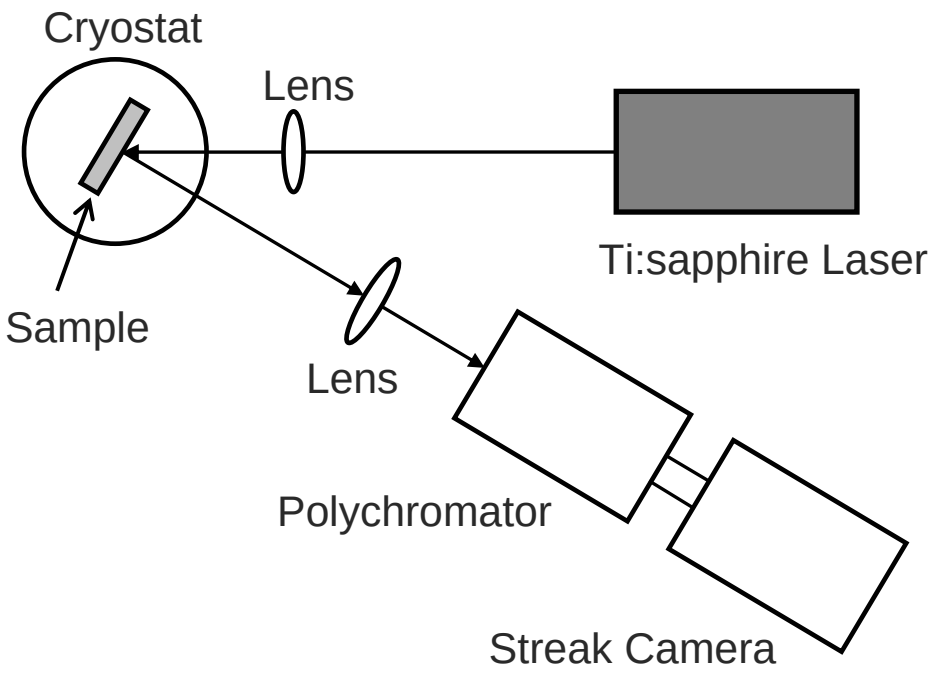
3. Time-resolved photoluminescence of excitons

- Time-resolved photoluminescence is powerful method to investigate directly relaxation and recombination process of excited carriers.

- 3.1 Free exciton emssions
  - relaxation process
  - radiative lifetime
  - temperature dependence of lifetime

- 3.2 Bound exciton emissions
  - radiative lifetime
  - charge state of defect centers

Measurement system of time-resolved PL



Ti:sapphire laser

wavelength	735～840nm (1.48～1.69eV)
pulse width	2ps
repetition rate	82MHz

Streak camera

time resolution	15ps

Measurement conditions

wavelength	766nm (1.62eV)
spot area	ϕ 1mm
excitation power density	0.1～2W/cm^2
temperature	10～50K

Measurement system of time-resolved PL

Picture of the measurement system

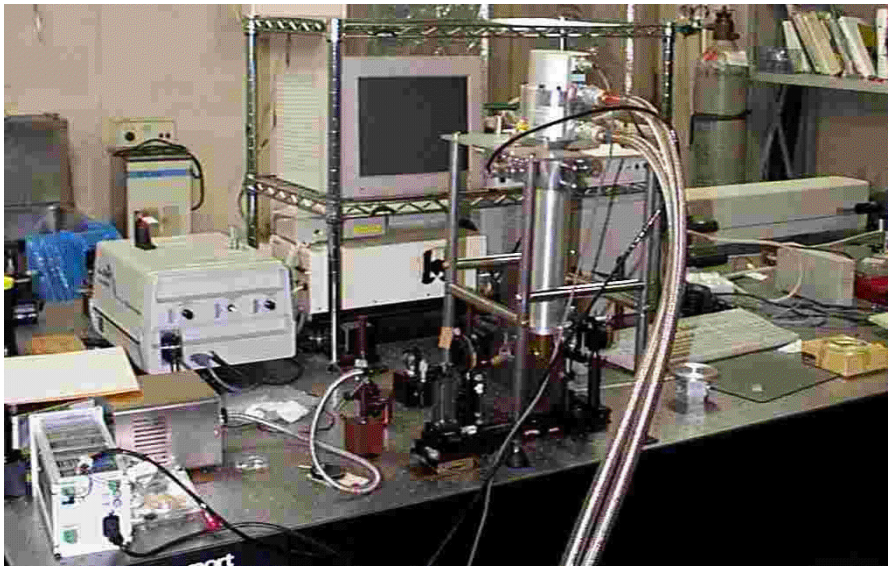
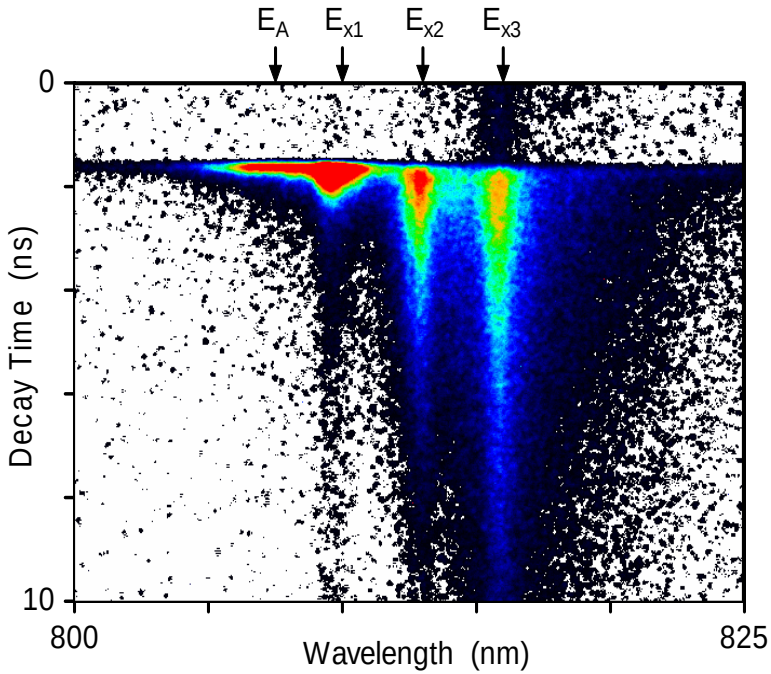
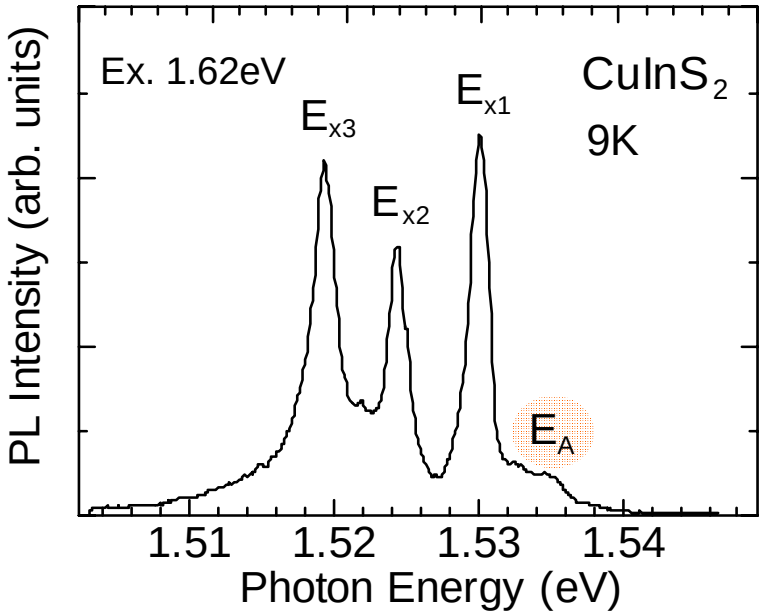


Image of obtained results using streak camera



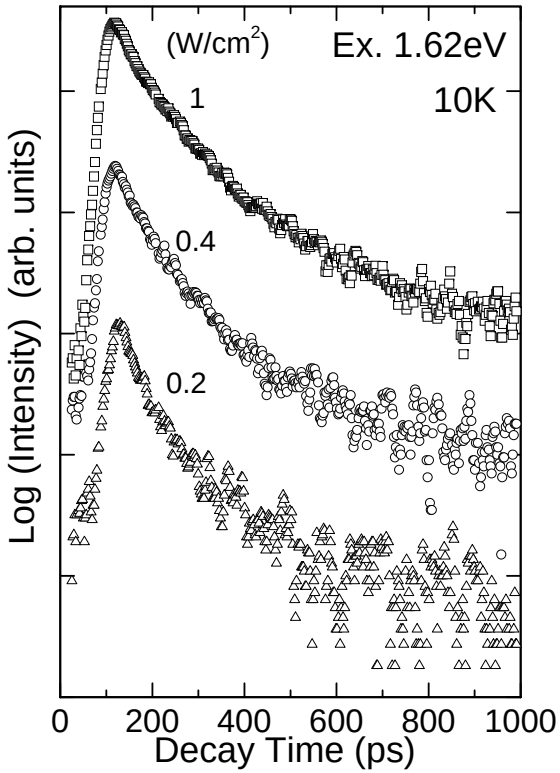
Photoluminescence spectrum

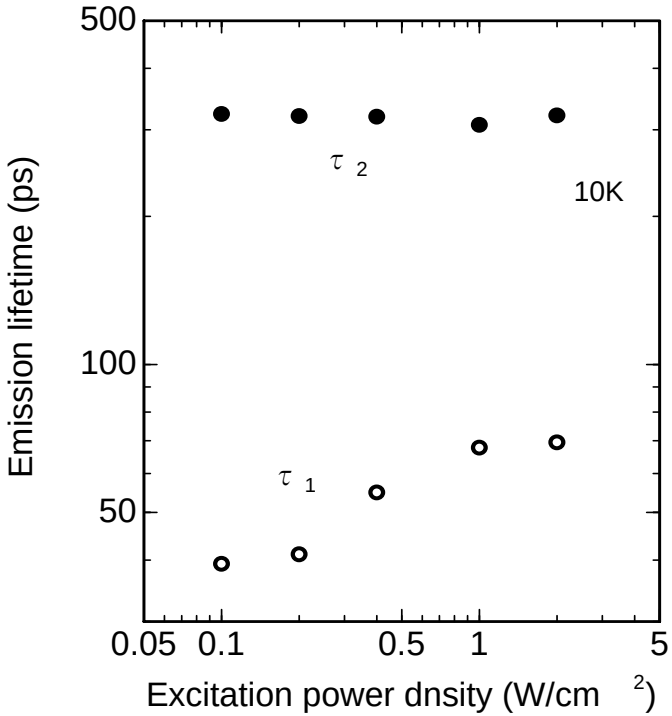
E_A	1.535eV	A free exciton
E_{x1}	1.530eV	bound exciton
E_{x2}	1.525eV	bound exciton
E_{x3}	1.520eV	bound exciton



- A shoulder (E_A at 1.535 eV) of a sharp peak (E_{x1} at 1.530 eV) in the higher-energy side is attributed to the A free exciton.
- In this work, we focus on the E_A emission of the A free exciton.

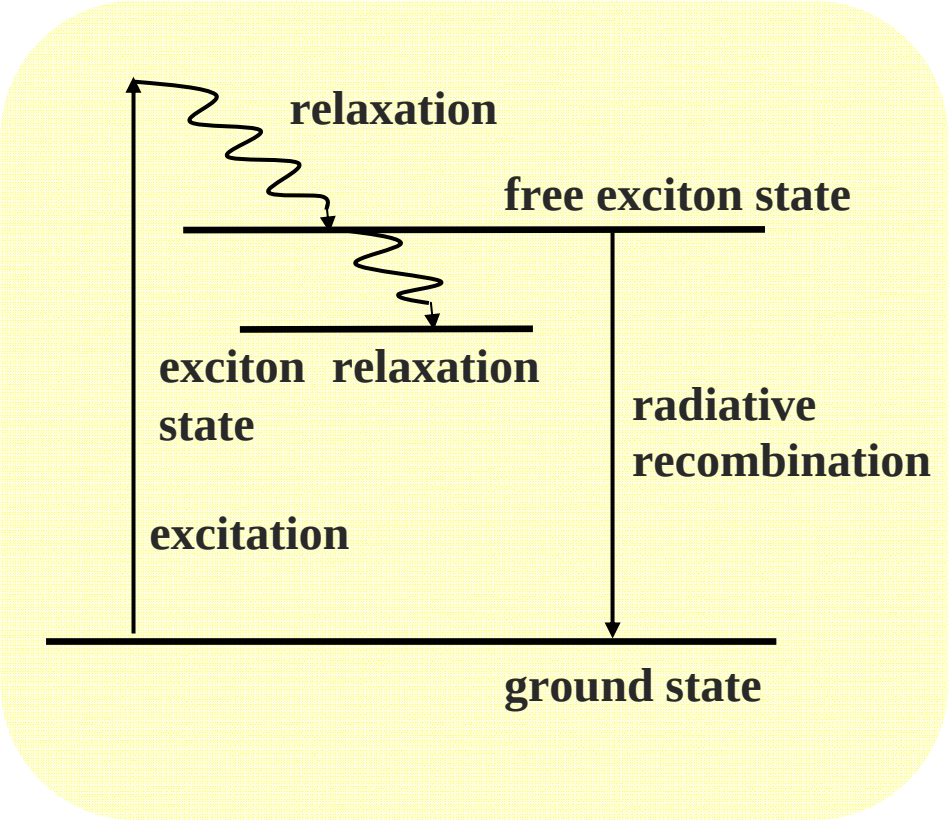
Decay carves of E_A emission





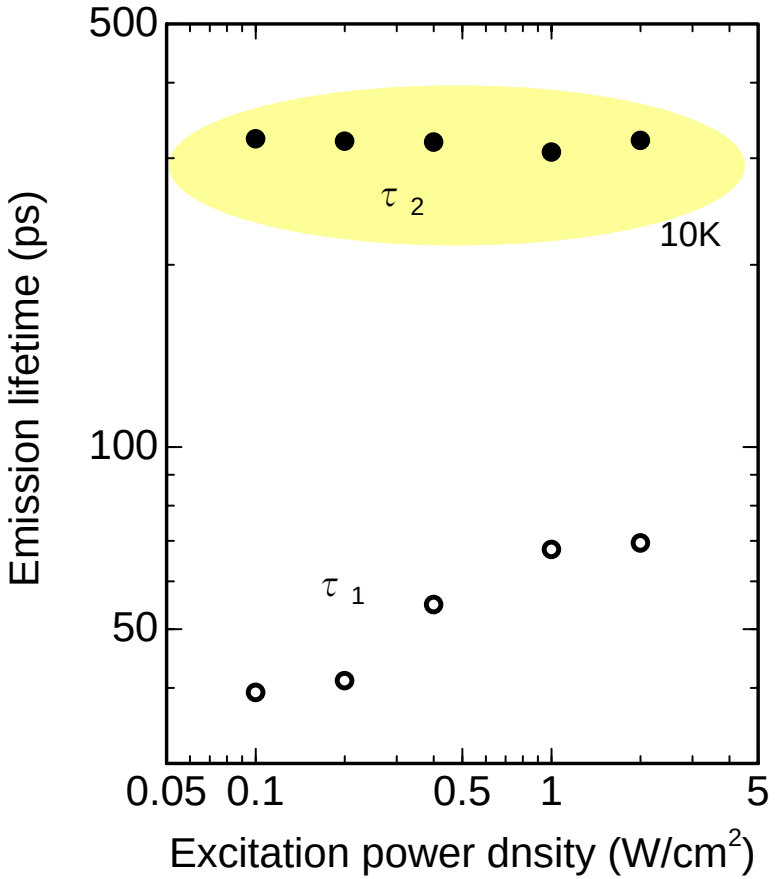
- The decay curves follow a double exponential. These curves indicate that decay is dominated by two distinct processes.
- The decay-time constant, τ_1 , of the fast component increases monotonically with increasing excitation intensity.

Relaxation model



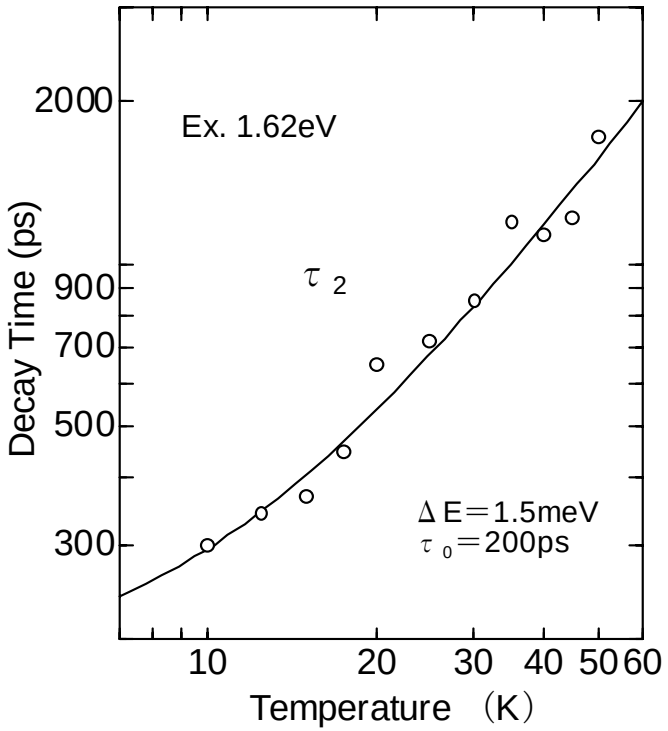
- The increase in τ_1 can be explained by the increase in the probability of the exciton relaxation states being occupied with excitation power, resulting in a lower probability of transition to the exciton relaxation state.
- The fast component of decay is dominated by nonradiative relaxation.

Excitation power dependence of decay-time constants



- τ_2 does not change with excitation power, indicating that the slow component is governed by radiative recombination.
- From this analysis, the radiative lifetime of the A free exciton is estimated to 320 ps at 10 K.

Temperature dependence of time-resolved free exciton emission



The fraction, r, of free excitons which have a kinetic energy below ΔE, is obtained by

$$r(T) = \frac{2}{\sqrt{\pi}(k_B T)^3} \int_0^{\Delta E} \sqrt{E} \exp(-E / k_B T) dE$$

where E is energy, T is temperature, and k_B is the Boltzmann constant. Therefore, the radiative lifetime vs. temperature is given by

$$\tau(T) = \tau_0 / r(T)$$

where τ_0 is constant.[R)]

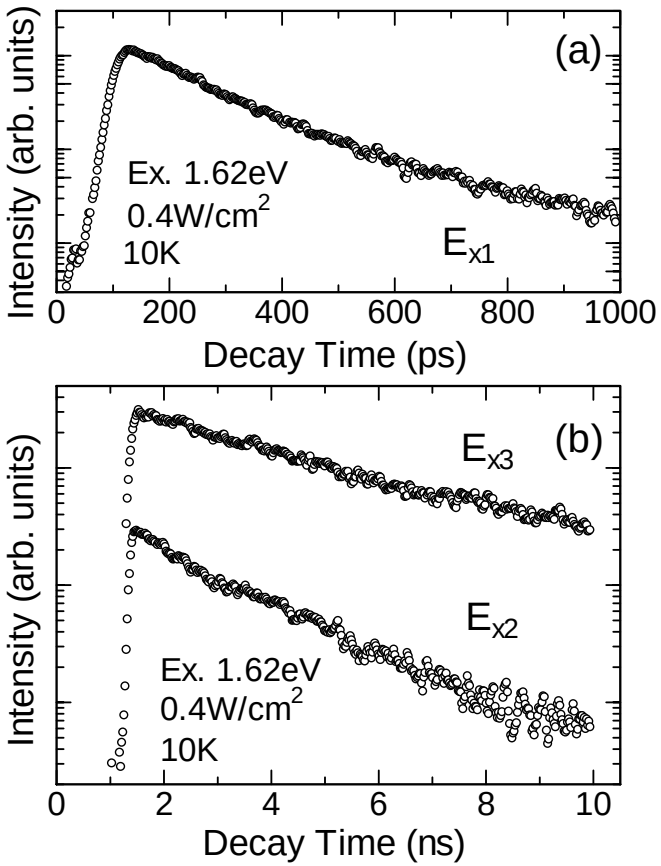
From the temperature dependence of τ_2 values, the radiative lifetime in the low-temperature limit is estimated to be 200 ps.

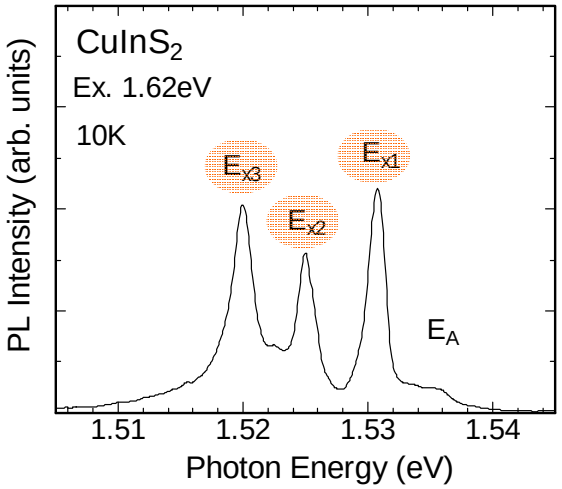
R) G. W. t'Hooft et al., Phys. Rev. B, 35 (1982) 8281.

Conclusion (2)

- Time-resolved photoluminescence of the A free exciton has been examined for bulk single-crystals of THM-$CuInS_2$.
- The decay of E_A emission follows a double exponential at low temperature, with decay-time constants τ_1 and τ_2; τ_1 increases monotonically with excitation intensity, whereas τ_2 is constant within an order of magnitude of excitation density.
- The fast and slow components of the decay curves are attributed to nonradiative relaxation and radiative recombination processes, respectively, and the radiative lifetime of the A free exciton was found to be 200 ps at lowest temperature limit.

Time-resolved photoluminescence of bound excitons





E_{x1}: double exponential curves

decay time-constant

fast component : 120 ps (τ_{1f})

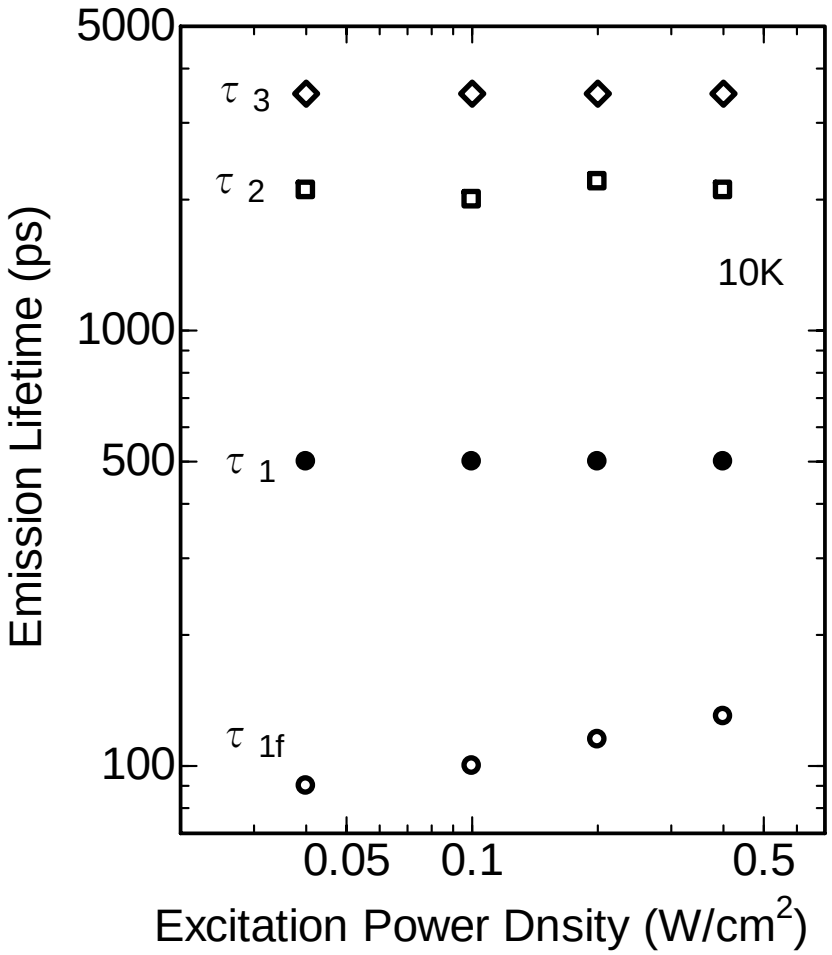
slow component: 500 ps (τ_1)

E_{x2}, E_{x3}: single exponential curves

decay time-constant

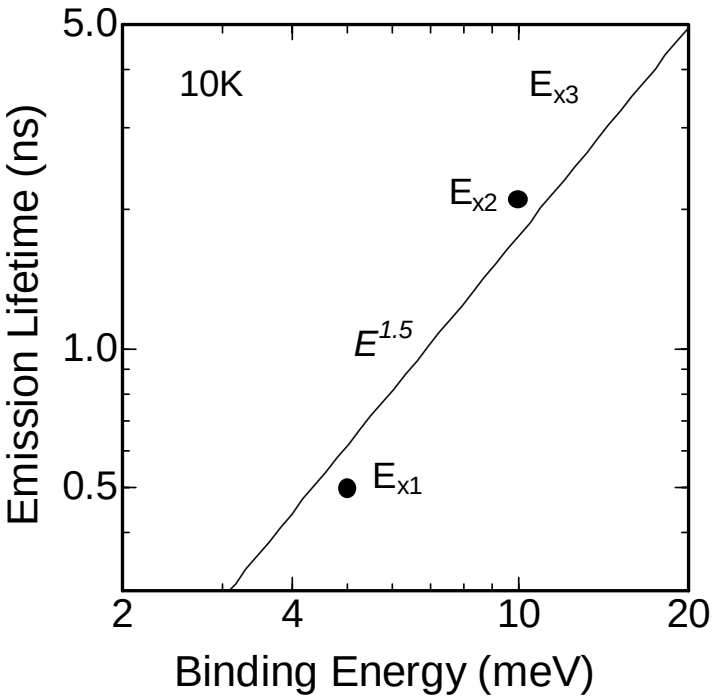
2.1 ns (τ_2), 3.5 ns (τ_3)

Excitation intensity dependence of decay time-constant



- The emission lifetimes, τ_1, τ_2, and, τ_3, were found to be almost constant and independent of the excitation power density that was varied in the range from 0.04 to 0.4 W/cm^2.
- It is reasonable to assume that the excitation density independent time-constants such as τ_1, τ_2, and τ_3 are the radiative lifetimes of the bound excitons E_{x1}, E_{x2}, and E_{x3}, respectively.

Binding energy vs. emission lifetime



- The obtained experimental values of the expectedly radiative lifetimes have been examined according to the theoretical equation[R)]

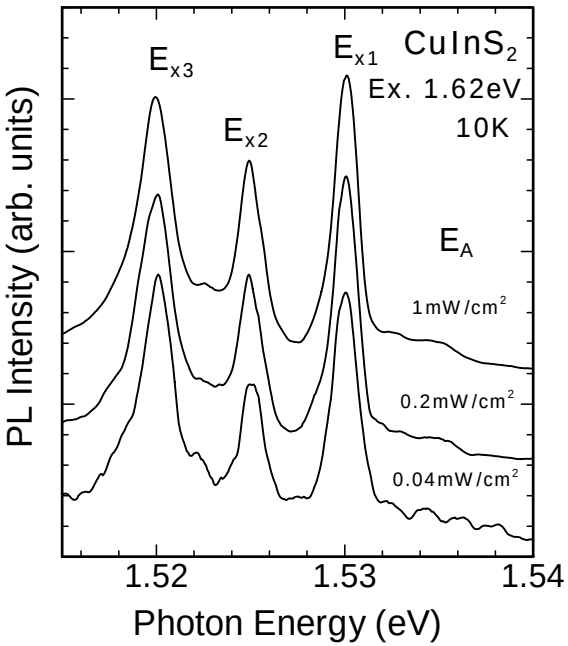
$$\tau_i \propto E_i^{1.5},$$

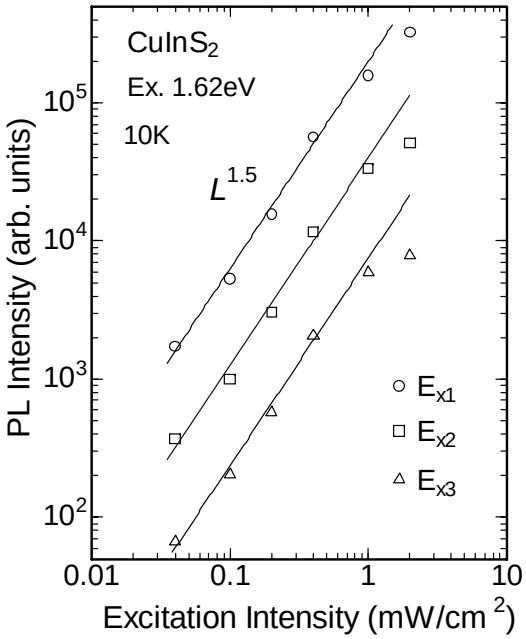
where E_i (i = 1, 2, 3) is the binding energy of a bound exciton E_{xi} (i = 1, 2, 3).

- Agreement with the theoretical equation is very good indeed, giving another strong argument in favor of the radiative nature of the τ_1, τ_2, and τ_3 time-constants.

R) E. I. Rashba and G. E. Gurgenishvili, Sov. Phs. Solid State **4**, 759 (1962). E. I. Rashba, Sov. Phs. Semicond. **8**, 807 (1975).

Excitation intensity dependence of bound exciton emissions





Bound exciton (E_{x1}, E_{x2}, E_{x3}) emission intensities increase as the 1.5 power of excitation intensity

Recombination of a complex

two electrons bound to one hole or two holes bound to one electron

E_{x1}, E_{x2}, E_{x3} are excitons bound to a neutral defect, (D^0,X) or (A^0,X).

Conclusions (3)

- We have examined the time-resolved PL of bound excitons in a bulk single-crystal of THM-grown $CuInS_2$ at 10K.
- The radiative lifetimes of the E_{x2} and E_{x3} emissions with single exponential decay have been estimated at 2.1 ns and 3.5 ns, respectively.
- Similar analysis of the slow component of the E_{x1} emission showing double exponential decay has given a radiative life time value of 500 ps.
- The charge state of the defect centers associated with the E_{x1}, E_{x2}, and E_{x3} bound excitons is argued to be neutral.

E. Analysis of exciton relaxation by time-resolved photoluminescence using pulse modulation method