# Possibility of coherent light emission from excitons in crystalline GaTe

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Free exciton photoluminescence (PL) spectra of crystalline GaTe has been studied as a function of continuous wave (cw) argon laser excitation intensity at $T=6$ K. When the excitation intensities are low ($P<4$ W cm$^{-2}$), the integrated PL intensities of free excitons for both singlet and triplet states increase approximately linearly with increasing excitation intensity. From about 4 to 9 W cm$^{-2}$, the peak energy redshift, the linewidth broadening, and the sharp increase of the integrated PL intensity of the exciton peaks are observed. These results are explained tentatively as large coherent emissions from excitons of GaTe. [S0163-1829(96)05424-0]

## I. INTRODUCTION

III-VI layered semiconductor compounds have potential for photoelectronic device applications. Recently, we studied the optical properties of one of this layered compound family, crystalline GaTe,[1–3] and observed the free ground-state singlet and triplet exciton peaks in the photoluminescence (PL) and transmission spectra at low temperatures and low excitation intensities. The free exciton peaks in the PL spectra of GaTe are well defined, have narrow linewidths, and are much stronger than the bound exciton peaks.[1] Therefore, this crystalline material supplies a good candidate for studying various phenomena such as collective radiations of free excitons. In this paper we report the dependence of free exciton PL spectra of GaTe on changing the cw excitation intensity. The possibility of the coherence of fluorescence photons emitted from excitons of GaTe is discussed, and the coherence of the exciton systems is monitored by observing the light emitted from them.

## II. EXPERIMENTAL RESULTS

Crystalline GaTe samples were grown by the iodine-assisted transport reaction technique.[4] PL measurements were made at $T=6$ K using an $Ar^+$ ion laser (514.5 nm) as a band-to-band cw excitation source. The excitation spot was about 700 $\mu$m in diameter and the excitation intensity was changed by a calibrated neutral density filter. The relative error of the laser intensity was less than 5%. The experimental details have been described previously.[1] The PL spectra of GaTe show two well-defined free exciton peaks, the ground-state ($n=1$) singlet $X_1$ and triplet $X_2$.[3]

When the excitation intensity $P<4$ W cm$^{-2}$, it can be seen from Figs. 1–3 that the peak energy position and the full width at half maximum (FWHM) of the two free exciton peaks ($X_1$ and $X_2$) remain almost unchanged. The singlet peak and the triplet peak are located at $X_1\sim1.7798$ eV and $X_2\sim1.7782$ eV, respectively, while their FWHM is $X_1\sim0.7$ meV and $X_2\sim0.6$ meV, respectively. From Fig. 4 we found that their integrated PL intensities ($I_{PL}$) increase with cw excitation intensity according to a power law

$$I_{PL}\propto P^S, \tag{1}$$

where the exponent $S$ is about 0.9 for the singlet $X_1$, and 1.0 for the triplet $X_2$. This behavior is typical of free exciton radiative recombination, and is observed experimentally in various semiconductors such as CdTe,[5] GaAs,[6] InSe,[7] and GaSe.[8–10]

When the excitation intensity $P$ varies from about 4 to 9 W cm$^{-2}$, the peak energies of the two free exciton states shift toward lower energies (Fig. 2), and the linewidths (FWHM) increase from about 0.7 to 1.4 meV for the singlet $X_1$ and from about 0.6 to 1.2 meV for the triplet $X_2$ (Fig. 3). In particular, the integrated PL intensities of excitons increase very rapidly (see Fig. 4) and the exponent $S$ of Eq. (1) is equal to 3.5 and 2.9 for the singlet $X_1$ and triplet $X_2$, respectively.

The emission of the singlet peak $X_1$ is linearly polarized perpendicular to the $b$ axis of crystalline GaTe, while the emission of the triplet peak $X_2$ is partially polarized parallel to the $b$ axis.[1] These polarization properties are also observed at relatively high excitation intensities for $P$ varying from 4 to 9 W cm$^{-2}$.

## III. DISCUSSION

Since the peak energies of free excitons in GaTe decrease while their FWHM increases with an increase in temperature,[2] it could be suggested that the redshift and broadening of the exciton peaks are caused by local heating effects. Using the radius of the excitation spot $\Delta x\sim350$ $\mu$m, an excitation intensity of $P\sim9$ W cm$^{-2}$, and the thermal conduction formula $P=\kappa(\Delta T/\Delta x)$, where $\kappa$ is the thermal conductivity of the materials and the minimum value of $\kappa$ for a typical bulk semiconductor at 6 K is $\sim0.1$ W cm$^{-1}$ K$^{-1}$,[11] we have estimated that the maximum local crystal temperature increase due to the heating effect of the laser excitation is $\Delta T=3-4$ K. Such a temperature increase will affect the exciton linewidth, the peak energy, and the PL intensity only slightly ($\sim10\%$).[2] However, if we suppose that the shift of the exciton peak energy is due completely to the thermal heating effect by the cw laser excitation and that the local temperature increase is porportional to the laser excitation intensity, we then obtain that the temperature increase due to laser excitation is about 22 K for $P\sim9$ W cm$^{-2}$ at the excitation spot (for a nominal crystal temperature of 6 K).

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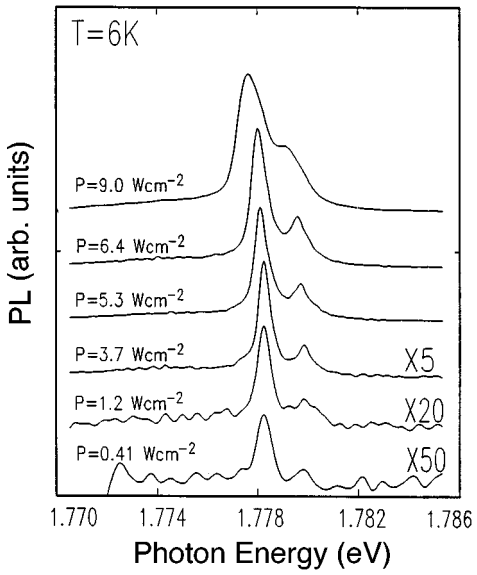


FIG. 1. The excitation intensity dependence of PL spectra for crystalline GaTe.

We therefore conclude that the peak energy redshifts, the linewidth broadenings, and the sharp increases of the integrated intensities of the free exciton $X_1$ and $X_2$ peaks cannot be attributed only to a thermal heating effect, and that a large part of the changes should be attributed to some other mechanism(s).

At low levels of laser excitation intensity, most photoexcited carriers and excitons are trapped nonradiatively by various impurities and defects inside crystals. If the densities of photoexcited carriers and excitons are comparable to that of the impurities, the depletion of the free exciton population due to the trapping of impurities is greatly suppressed. This results in sharp increases in the exciton PL intensities. For the present study, the photon energy of excitation is $\sim 2$ eV, and the exciton and carrier lifetimes in crystalline GaTe are about 100 ps,[3,4] the absorption coefficient is assumed to be about $10^3$ cm$^{-1}$, then we found that the densities of photoexcited carriers and excitons in GaTe crystals are about $\delta n \sim 10^{12}$–$10^{13}$ cm$^{-3}$ when the excitation intensity is about 4 W cm$^{-2}$. These photoexcited carrier and exciton densities are at least 1000 times smaller than the impurity concentration, which is about $10^{16}$ cm$^{-3}$, in GaTe crystals grown by the iodine-assisted transport reaction technique.[12] Therefore, the sharp increases of integrated exciton PL intensities could not be caused by the saturation of impurities by photoexcited carriers and excitons in the crystals.

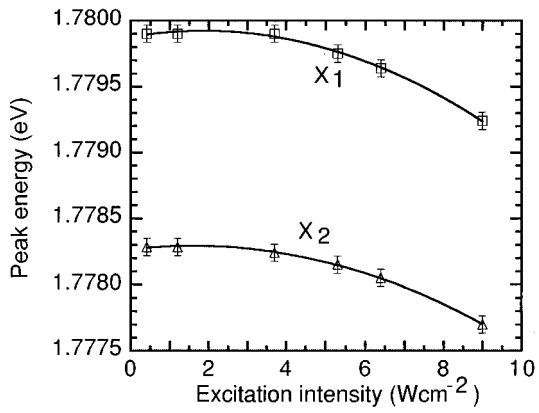


FIG. 2. The peak energy variation of singlet peak $X_1$ and triplet $X_2$ with laser excitation intensity. The solid lines are fitting curves.

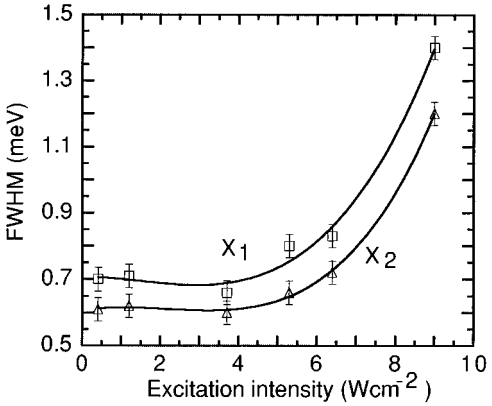


FIG. 3. The variation of FWHM with laser excitation intensity. The solid lines are fitting curves.

Given the crystal temperature of 6 K and the low exciton density ($10^{12}$–$10^{13}$ cm$^{-3}$), the explanation for sharp increases of the integrated exciton PL intensities (for $P$ above $\sim 4$ W cm$^{-2}$) based on Bose-Einstein condensation is also unlikely. The estimated critical temperature for the transition is $\sim 2$–$3$ mK and is much lower than 6 K.[13]

Although the cubic PL intensity dependence on excitation intensity has been established for electron-hole ($e$-$h$) drop and plasma recombinations,[14,15] which are observed in highly photoexcited semiconductors, an explanation based on these two models is also apparently not suitable. The Mott density of excitons in GaTe is about $10^{17}$ cm$^{-3}$ (Refs. 16 and 17) and is much larger than the present $e$-$h$ pair density of $10^{12}$–$10^{13}$ cm$^{-3}$. Also the $e$-$h$ drop and plasma recombinations give new PL peaks located at the lower-energy side of the free exciton peaks in III-VI layered compounds.[18,19]

The sharp increases of the integrated PL intensities for the two exciton peaks above $P \sim 4$ W cm$^{-2}$, together with the apparent redshifts of their peak energy positions, and the broadenings of their linewidths (FWHM), would suggest coherent emission processes from the excitons of GaTe. This is discussed in the following.

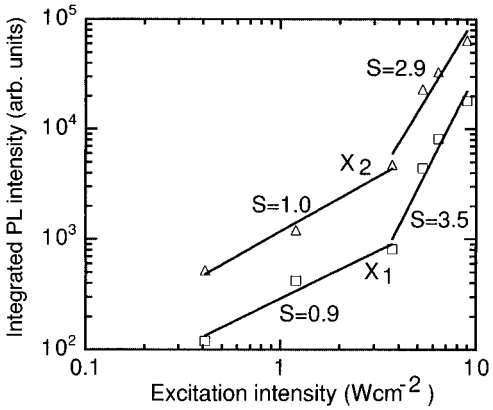


FIG. 4. The change of integrated emission intensities of singlet peak $X_1$ and triplet peak $X_2$ with laser excitation intensity. The solid lines are fitting curves.

The radiative emission of singlet excitons is linearly polarized perpendicular to the *b* axis of crystalline GaTe, and the radiative emission of triplet excitons is partially polarized parallel to the *b* axis.[3] These polarized properties of emissions supply a more advantageous condition for the coherence of optical fields emitted by these excitons than the unpolarized emissions of excitons, since the electrical components of optical fields vibrate along the same directions. It meets one of the three requirements for a realization of the coherence of light. Also, the very narrow linewidths of the exciton PL peaks (the linewidth over peak energy is only $\Delta E/E \sim 3\times 10^{-4}$ for singlet or triplet PL peaks) could well satisfy the so-called ''single frequency'' requirement for the coherence of light. The final condition for the phase correlation of the light fields is also possible: the exciton lifetimes are $\sim$100 ps in this GaTe material,[3] and free excitons in bulk semiconductors move typically with velocities of about $10^6-10^7$ cm s$^{-1}$. Then, the maximum distance the excitons could travel during their lifetimes is about $10^4-10^5$ Å, which is comparable to or larger than the mean distance between excitons ($\sim 10^4$ Å) obtained from an exciton density of $10^{12}-10^{13}$ cm$^{-3}$. It is very likely that increasing the excitation intensity above a critical value of 4 W cm$^{-2}$ will largely increase the collision (interaction) probability between excitons. The exciton-exciton interaction could make the phase correlation between excitons possible. That is, the wave functions of excitons may now be correlated. The phases of emitted light are determined by the phases of the wave functions of the excitons. The fluorescence photons emitted at different times or locations could be correlated to each other as long as the wave functions of the exciton states are coherent.[20] The coherence in the light fields may result in the coherence in the excitons, and the coherence in the excitons may result in coherent radiation. The coherence in the excitons and in the photon fields emitted by exciton recombinations may transfer from one to another. The large increase of fluorescence light for excitation intensity about $P>4$ W cm$^{-2}$ could be a measure of the coherences in both the light fields and the exciton systems of crystalline GaTe.

At the low excitation intensities $P<4$ W cm$^{-2}$, although the light emissions from exciton recombinations are polarized and have narrow linewidth, the interaction among excitons is probably negligible so that the phases of exciton wave functions are not correlated and are independent of one another. The fluorescence photons emitted by these excitons are therefore not correlated. This is why at the low excitation intensities ($<4$ W cm$^{-2}$), we do not observe the coherent emissions of excitons.

When comparing the linearly polarized emission from singlet excitons with the partially polarized emission from triplet excitons, the coherent phenomenon is expected to be stronger for the singlet PL peak than that for the triplet PL peak; this is exactly what we observed experimentally (see Fig. 4). The exponent $S$ of Eq. (1) for the singlet peak $X_1$ ($S\sim 3.5$) is larger than that for the triplet peak $X_2$ ($S\sim 2.9$) when optical excitation rises above a critical intensity of $P \sim 4$ W cm$^{-2}$. This observation supports the picture of coherent radiations by singlet and triplet excitons.

The redshift of exciton peak energies and their linewidth broadening at $P>4$ W cm$^{-2}$ also support the exciton-exciton interaction picture. The interaction among excitons results in higher effective exciton temperatures above the nominal crystal temperature of 6 K.[3,19] These excitons are said to be in a ''hot,'' nonthermalized state. We thus observe the energy redshifting and the linewidth broadening of exciton PL peaks with increasing excitation intensity for $P>4$ W cm$^{-2}$.

Therefore the polarized emissions, the narrow PL linewidths, and interactions among excitons are the main reasons for the observed behavior of the free exciton PL peaks in crystalline GaTe for a cw excitation intensity $P$ varying from $\sim$4 to 9 W cm$^{-2}$. Unfortunately, we cannot increase a cw excitation to much higher levels since the samples could be heated locally and burned out. In order to increase the excitation levels while avoiding the burning effect, we normally use pulsed excitations.[3] It would be interesting to study the excitation intensity dependence of free exciton PL spectra of GaTe at higher excitation levels using pulsed excitations; this is a task to be accomplished in the future.

There is a possible super-radiant emission from the excitons.[20] The super-radiant state is now formed by excited excitons located within a distance less than the wavelength of light, and we cannot define the exciton that emits the light.[20] When the exciton system is in a super-radiant coherent state, it is known that the fluorescence intensity is proportional to the square of the number of excitons, which is roughly proportional to the excitation intensity. However, it could be important to take propagative effects into account. When the super-radiant emission propagates through the crystalline materials and the light may be amplified or deamplified depending on the relative phase between the light and the exciton system at each local area,[20] this may result in a larger exponent than $S=2$.

## IV. CONCLUSIONS

Free exciton PL spectra of crystalline GaTe are studied as a function of cw excitation intensity at a nominal crystal temperature of $T=6$ K. Below $P\sim 4$ W cm$^{-2}$, an almost linear change of the integrated intensity of the excitonic emission peaks is observed with increasing $P$. From about 4 to 9 W cm$^{-2}$, we observe superlinear increases of the integrated PL intensities for both the ground-state ($n=1$) singlet and triplet exciton peaks with an exponent $S\sim 3.5$ and 2.9, respectively. The increases of exciton PL intensities are accompanied by apparent peak energy shifts toward lower energies and increases in the linewidth (FWHM). These results are tentatively attributed to large coherent emissions from exciton systems, caused by the polarized properties of the emissions, the narrow PL linewidths, and the interactions among excitons. The possibility of transfer of the coherence between the photon fields and the exciton systems is proposed. More experimental and theoretical work is needed to further verify this collective radiation picture.

## ACKNOWLEDGMENTS

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