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Anti-Stokes luminescence in the light of second order perturbation theory

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Anti-Stokes photoluminescence is measured in high-quality GaAs quantum wells. The primary pathway for interband optical absorption and hence emission under subbandgap photoexcitation is the optical phonon-mediated second-order electric dipole transition. This conclusion is drawn from the remarkable agreement between predictions of second-order perturbation calculation and the measured intensity of anti-Stokes photoluminescence, both as function of the detuning wavelength and temperature. The results are of direct relevance to laser cooling of solids where phonon-assisted upconversion is a necessary condition. © *2014 AIP Publishing LLC*.
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Anti-Stokes photoluminescence (ASPL) or luminescence upconversion refers to a blue-shift in the spontaneous emission with respect to the excitation energy. Two-photon absorption,[1] Auger recombination,[2] and absorption of phonons[3] are among the many pathways, which may lead to upconversion. Of lively interest is the upconversion mechanism where the carriers absorb phonons from the system and efficiently release the extra energy through photons, possibly cooling the lattice.[4–11]

We experimentally study ASPL in high quality GaAs quantum wells. Although ASPL has been previously studied in semiconductors, including GaAs quantum wells,[3,12–21] experimental data have so far been analyzed without a generic theoretical framework. The mechanism of ASPL has been shown to be two-step absorption[12–16,20] by localized carriers,[13,16,20] including excitons,[12] involving defect states[15] and other intermediate states,[21] and phonon-assisted transitions.[3,10] A reasonably detailed experimental study on GaAs has already been reported in Ref. 3 but the analysis in that work was largely empirical without any insight into the microscopic quantum mechanical processes involved in carrier photoexcitation.

One would imagine that at least in high quality samples, the fundamental process involved in optical interband absorption under subbandgap laser excitation is the simultaneous absorption of a photon and a phonon.[10] It thus seems natural to formulate the problem using second-order perturbation theory (with the electron-phonon and the electron-photon interactions each contributing one order to the perturbation), in analogy with the theory for interband absorption in indirect gap semiconductors.[22] We do so here and confront theory with experiment.

A molecular-beam-epitaxy-grown high-quality GaAs/AlGaAs multi-quantum well sample containing 20 GaAs quantum wells, each 8 nm wide, separated by 15 nm wide $Al_{0.33}Ga_{0.67}As$ barriers was mounted in optical closed-cycle helium cryostat. A wavelength tunable Ti:Sapphire laser was used in continuous-wave mode to excite the sample. The emission spectra were dispersed in a grating spectrograph ($f = 0.5$ m) connected to a silicon charge-coupled device detector. Fig. 1 shows (the usual "Stokes") photoluminescence (PL) spectra measured at 10 K and 100 K, respectively, under 2 mW excitation power at an excitation energy of 1.63 eV (indicated by an arrow).

For ASPL measurements, the sample was excited at an energy lower than the PL peak energy with a 20 mW laser beam focused to spot-size of $\sim 75\,\mu$m in diameter. Measurements were performed for several values of detuning Δ of the excitation laser and for temperatures ranging from 10 K to 220 K. ASPL was too small to be detected below 10 K. A representative set of detuning-dependent ASPL spectra measured at 100 K is shown in Fig. 2. Expectedly, the ASPL intensity monotonically decreases with increasing detuning.[3] Note that while the light-hole exciton (lh-x) peak ($\sim$1.564 eV) and the onset of $n = 1$ subband also become visible in the PL spectra at high temperature, we will only be focussing on the heavy-hole exciton (hh-x) transitions ($\sim$1.546 eV) in this study.

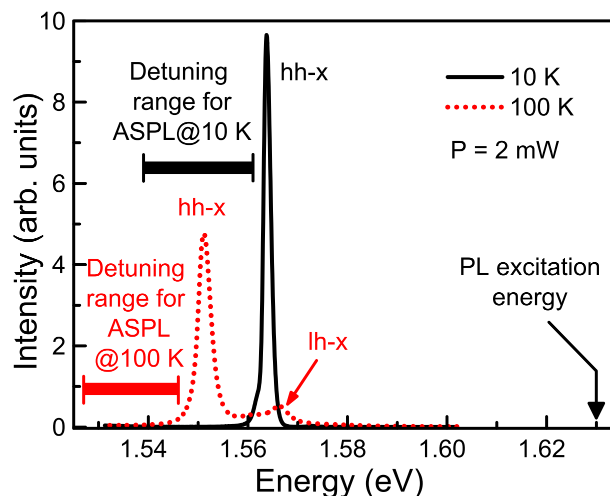

FIG. 1. PL spectra of our GaAs multi-quantum well sample at 10 K and 100 K under 2 mW laser excitation at an energy of 1.63 eV (indicated by an arrow). The range of detuning used for ASPL measurements at these temperatures is also indicated.

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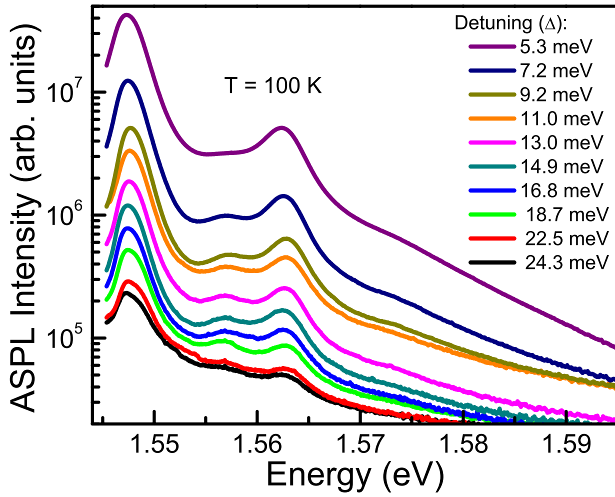

FIG. 2. Detuning dependent ASPL spectra at 100 K. The detuning values shown in the legend are in the same order as the spectra appear with decreasing intensity, i.e., the spectrum with highest intensity corresponds to the first detuning in the legend and so on.

In Fig. 3, the peak intensities of the heavy-hole ASPL spectra are plotted on logarithmic scale as a function of detuning for a wide range of temperatures. Particular symbol denotes a specific temperature. It is perhaps reasonable to assume that the primary dependence of the radiative efficiency comes from the temperature and not from the detuning, since nonradiative processes typically have an activation barrier giving them an exponential temperature dependence. Hence, to compare the detuning-dependence of ASPL intensity measured at different temperatures, each of these datasets has been scaled by a constant multiplier such that all of them have almost the same intensity near $\Delta = 10$ meV. Somewhat surprisingly, the data—spanning over two orders of magnitude in intensity and measured in a temperature range of 10–220 K—all now nearly merge onto a single curve in Fig. 3. This suggests that the ASPL intensity can be described by a universal function of detuning.

The simplest mechanism for phonon-assisted ASPL is qualitatively similar to that of the phonon-mediated indirect interband transitions. Within the second order perturbation theory picture, the valence band electrons are promoted to the conduction band via a (sum of many) two-step process(es) with virtual intermediate states. This calculation of the transition rates w for indirect optical transitions gives[22]

$$w = \frac{2\pi}{\hbar}\sum_{if}\sum_{m}\frac{|M_{fm}^{\rm phon}|^2|M_{mi}^{\rm phot}|^2}{(\varepsilon_m-\varepsilon_i-\hbar\omega)^2}\delta(\varepsilon_f-\varepsilon_i-\hbar\omega-\hbar\omega_q). \quad (1)$$

where i, f, and m stand for the initial, final, and intermediate states and ε_i, ε_f, and ε_m are the energies corresponding to those states, respectively. The above equation describes the processes where the system first gets excited with incident photon of energy $\hbar\omega$ to the intermediate state and then absorbs a phonon of energy $\hbar\omega_q$ to reach the final state. The other set of pathways where a phonon is absorbed first is less likely by a factor $\sim[\omega_q/\omega]^2 \sim 5\times10^{-4}$ from the energy denominator and is therefore safely ignored. $M_{mi}^{\rm phot}$ and $M_{fm}^{\rm phon}$ are the matrix elements for electron-photon and electron-phonon coupling respectively. $|M_{mi}^{\rm phot}|^2$ is constant for vertical transition (wave vector $k=0$) and gives an overall factor of ω in the denominator. $|M_{fm}^{\rm phon}|^2$ can be written in general as $\aleph(q)n_q$ for phonon absorption, where $\aleph(q)$ is a coupling parameter, which, in general, is a function of phonon wave vector q. n_q is the Bose distribution

$$n_q = \frac{1}{\exp(\hbar\omega_q/k_BT)-1}. \quad (2)$$

The form of $\aleph(q)$ depends upon the type of phonons (acoustic or optical) and the nature of coupling (deformation potential or Fröhlich interaction). It is easy to argue that acoustic phonons cannot participate in the upconversion process, and only optical phonons are involved. Suppose an electron is excited with incident photon energy $\hbar\omega$ (below E_g) and it subsequently absorbs an acoustic phonon of energy $c_p\hbar q$, where $c_p\hbar$ is the slope of the acoustic phonon dispersion curve. If the energy provided by the acoustic phonon is sufficient, then the electron gets promoted to the conduction band and can also acquire some kinetic energy. Under parabolic approximation for the conduction band, we can write

$$\hbar\omega + c_p\hbar q = E_g + \frac{\hbar^2q^2}{2\mu}, \quad (3)$$

which demands the following condition to be satisfied for real solution of q:

$$E_g - \hbar\omega = \Delta \le \frac{1}{2}\mu c_p^2. \quad (4)$$

The above argument is pictorially presented in Fig. 4. With the reduced mass $\mu \sim 0.05m_0$ for GaAs and the estimated value of c_p from GaAs phonon dispersion curve we get an upper bound of $\Delta \sim 10^{-2}$ meV. Here, m_0 is the free electron mass. We have observed ASPL for more than 25 meV of detuning. The argument shows that this can only happen by absorbing optical phonons.

Hence, one needs to only consider optical phonon scattering in evaluating Eq. (1). With this in mind, let us make a zeroth-order back-of-the-envelop estimate of the absorption

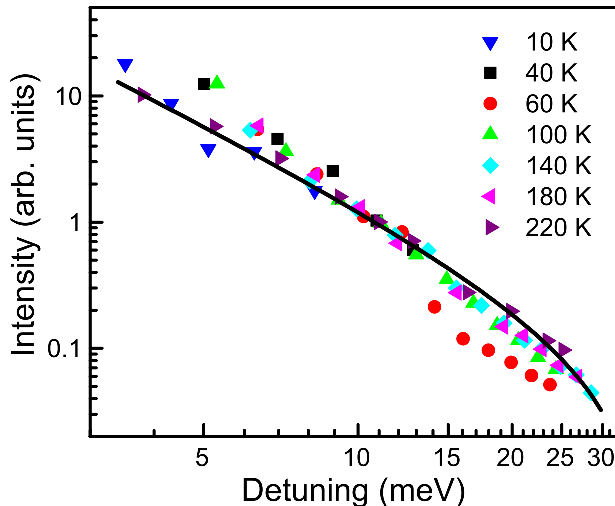

FIG. 3. Scaled intensities of ASPL measured at different temperatures are plotted as a function of detuning on logarithmic scale. The solid line represents the fit to the data by the detuning-dependent factor in Eq. (5).

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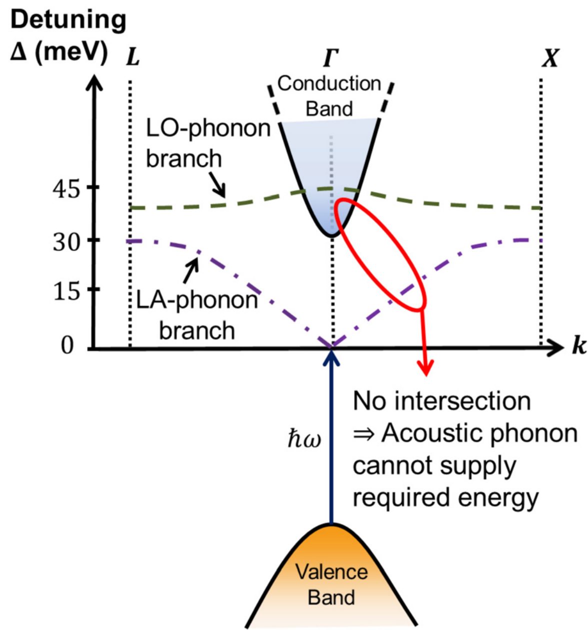

FIG. 4. Schematic description of the fact that acoustic phonons cannot contribute to ASPL. The solid line and the dashed-dotted curves and the dashed line are, respectively, the electron, acoustic phonon, and optical phonon dispersion curves for GaAs. For real solution of q, the acoustic phonon dispersion curve [dashed-dotted line, corresponds to the left hand side of Eq. (3)] and the electron dispersion [conduction band parabola drawn by the solid line, corresponds to the right hand side of Eq. (3)] should cross each-other. But the band structure of GaAs does not permit that for acoustic phonons, except for very small detuning. Optical phonons have their dispersion (dashed line) crossing the electronic conduction band and can provide required energy for fairly large values of detuning.

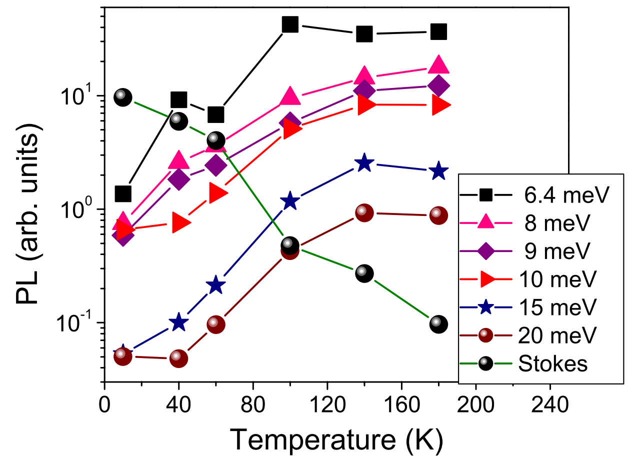

FIG. 5. ASPL at the heavy-hole exciton resonance at different temperatures for detuning energy between 6.4 to 20 meV corresponding to the heavy hole exciton resonance at the given temperature. The temperature-dependent (Stokes) PL intensity is also shown and it is arbitrarily scaled so that all the data fit the same graph.

coefficient $\alpha(\omega) \equiv w/[Ncn]$. Here, w is given by Eq. (1), N is the number density of photons, c the velocity of light, and n the refractive index. Equation (1) is considerably simplified by (i) assuming that optical phonons in GaAs have flat dispersion with a constant energy of 36 meV, (ii) ignoring the wave vector dependence $\aleph(q)$, and (iii) $\varepsilon_m - \varepsilon_i$, the difference in the energy between the initial state "i" in the valence band and the intermediate state "m" in the conduction band is equal to the energy gap E_g. Then, the energy denominator in Eq. (1) becomes $[E_g - \hbar\omega]^2 = \Delta^2$, which can be taken out of the summation. Note it is standard to make a similar approximation in deriving the expression for optical absorption in indirect gap semiconductors.[22,23] The essential energy dependence in the expression for the absorption coefficient then comes from the two-dimensional density of states that appears in the conversion of the summations into phase space integrals. The final approximate expression for $\alpha(\omega)$ is

$$\alpha(\omega) \approx \frac{4e^2|\vec{\epsilon}\cdot\vec{p}^{\,0}_{cv}|^2\aleph}{m_0^2 cn\hbar^4}\left(\frac{\hbar\omega_L - \Delta}{\omega\Delta^2}\right)\left[\frac{1}{\exp\left(\frac{\hbar\omega_L}{k_B T}\right) - 1}\right] \quad (5)$$
$$= [\text{constant}] \times f(\Delta) \times g(T).$$

Here, $\vec{\epsilon}$ and $\vec{p}^{\,0}_{cv}$ are polarization vector and transition matrix element (for vertical transition, i.e., $k = 0$) for the momentum vector of photon, respectively, $\hbar\omega_L$ denotes the optical phonon energy. According to Eq. (5), phonon-mediated interband absorption coefficient is expected to have a specific dependence on detuning [$f(\Delta)$] and temperature [$g(T)$]. PL intensity is proportional to the spontaneous emission rate and the carrier distribution functions in the valence and conduction bands. As the absorption coefficient is related to the spontaneous emission rate through the relationship between the Einstein A and B coefficients,[24] the temperature and detuning dependence of the PL and the absorption coefficient should essentially follow each other.

The solid line in Fig. 3 shows the detuning dependence [$f(\Delta)$, with $g(T)$ fixed] expected from Eq. (5). Indeed, the detuning-dependent factor of Eq. (5) very well fits the experimentally measured ASPL intensity versus detuning data in Fig. 3 over more than two orders of magnitude of intensity. The only adjustable parameter for fitting is a constant prefactor. Note that the above considerations are based on free electrons and holes, without accounting for any excitonic features. This seems reasonable because of the much larger phase space associated with the free electron and hole states.

Finally, let us check the temperature-dependent factor in Eq. (5). The emission intensity is strongly dependent on temperature (Fig. 5), but here, the primary factor affecting the intensity would be the loss through various non-radiative channels, which are not easily accounted for in theory. To make sense of the data in Fig. 5, let us (approximately) cancel the temperature dependence of this nonradiative contribution in PL by taking the ratio of ASPL to Stokes PL intensity at each temperature. This procedure assumes that the reduction in the strength of the band-edge emission due to nonradiative processes is constant at a given temperature, independent of where in the band the carriers are created. Fig. 6 shows such temperature-dependent relative ASPL intensity data (normalized to the T = 180 K data) for several values of detuning along with the Bose factor appearing in Eq. (5), for a constant optical phonon energy of 36 meV. As evident from the semilogarithmic plot in Fig. 6, the phonon distribution function nicely fits the data over nearly three orders of magnitude. Here also, a constant prefactor is taken as the only adjustable parameter to fit the data. This figure not only shows a good agreement between the prediction of Eq. (5) and our data, but it also proves that the ASPL

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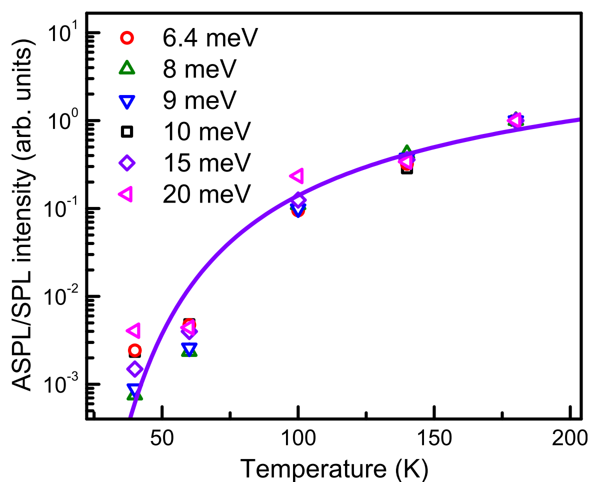

FIG. 6. Semilogarithmic plot of ratio of the ASPL intensity to the PL intensity as a function of temperature for various values of detuning. The intensities for different detunings are normalized to one at 180 K. Solid line is the optical phonon distribution function [Eq. (2)] for GaAs up to a constant prefactor.

mechanism in our experimental configuration does involve optical phonons.

To summarize, we have studied the fundamental physics of ASPL in GaAs quantum wells in a wide range of temperatures, 10–220 K, up to a large value of 30 meV of laser detuning. Dependence of the ASPL intensity on the detuning and temperature were independently studied. An estimate of the total absorption cross section for the below-bandgap photons, as a function of these two fundamental parameters, could be made on the basis of the experimental results. We found that all the results could be very well-described within the second order perturbation theory for phonon-assisted optical transitions, similar to the one used for describing interband absorption in indirect gap semiconductors. The calculations were not specific to the particular GaAs quantum well sample used here; they should be applicable for understanding ASPL emission efficiency in any two-dimensional system, and with a modification in Eq. (5) (using appropriate density of states) to any high quality band insulator. Despite the phonon-assisted ASPL, we did not observe any net cooling. High background absorption from the bulk GaAs substrate perhaps caused extra heating that dominated over the ASPL cooling.

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