AUGER RECOMBINATION OF EXCITONS BOUND TO NEUTRAL DONORS IN GALLIUM PHOSPHIDE AND SILICON

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The lifetimes of excitons bound to neutral donors in GaP and Si were measured to be much shorter at low temperatures than predicted from absorption measurements. An Auger recombination process in which one bound electron recombines with the bound hole while exciting the second bound electron into the conduction band is believed to predominate over radiative recombination.

The so-called *C* line in the luminescent spectrum of GaP arises from the radiative recombination of an exciton bound to a neutral donor believed to be sulfur.[1,2] From absorption measurements on the line on crystals of known S concentration[1] the cross section integrated over the emission frequencies was found to be 7×10^{-21} cm^{-2} eV, accurate to about a factor of 2.[3] Since the *C* line is a resonance line,[2] the radiative lifetime τ can be found from detailed balance using

$$\tau^{-1}=\frac{8\pi n^2 g_1}{\lambda^2 g_2}\int\sigma d\nu, \qquad (1)$$

where $g_1=2$ is the degeneracy of the neutral S donor state, $g_2=4$ is the degeneracy of the state representing the exciton bound to the neutral S donor,[2] $\lambda=5367$ Å (1.6°K) is the wavelength, $n=3.47$ is the index of refraction, and $\int\sigma d\nu$ is integrated cross section. Equation (1) then yields a predicted radiative lifetime of 11 μsec. We have measured the decay lifetime of the *C* line at low temperatures (1.6 and 4.2°K) where thermal ionization of the center is negligible, using pulsed electron-beam excitation described previously.[4] It was found to be 21 ± 4 nsec, which is about 500 times shorter than the predicted value.

Several possible explanations of this absorption-emission discrepancy are conceivable. (1) Another impurity, or perhaps interstitial or paired S atoms, are present in the crystals at a concentration of 1/500 of the substitutional S concentration and the *C* line is really associated with that impurity. [Zeeman data[2,5] show that any such impurity must be a donor.] (2) There is radiation at other frequencies than those considered so far which decreases the lifetime. (3) The dominant decay is nonradiative.

Many crystals, grown by a variety of techniques and doped with S both intentionally and unintentionally, have been studied in emission and absorption and have given consistent results. The involvement of a second and uncontrolled impurity thus seems highly unlikely. Involvement of interstitial S atoms as the binding centers is also unlikely since this hypothesis would create the problem of why we do not observe a much stronger "*C* line" which would be associated with substitutional S atoms. Paired *S* atoms can be ruled out by the Zeeman data,[2,5] which indicate that the binding center is a point defect. The second possibility—the presence of radiation at other frequencies—can be ruled out because of the weakness of the phonon-assisted satellite lines of the *C* line. These vibronic transitions have been observed in absorption[1] and emission[6] and found to have an integrated strength of only 6%[6] of the *C* line and so cannot explain the huge discrepancy in the detailed balance calculation of Eq. (1).[7]

We conclude that the decay of this bound-exciton complex proceeds mainly by a nonradiative process. This complex consists of a positively charged S atom on a P site to which are bound two electrons and one hole. Radiative recombination of one of the electrons with a hole yields a photon at the *C*-line frequency. We believe a much more probable recombination mechanism is an Auger process in which one of the electrons and the hole recombine giving their energy to the second electron, which is freed into the conduction band and dissipates its excess kinetic energy through collisions with the lattice.

The theory of the relative probabilities of the Auger and radiative processes has many similarities to the calculation of the internal conversion coefficient of nuclear physics.[8] Thus a rough estimate of the ratio of the probabilities of the Auger process to the radiative process can be obtained from the internal conversion coefficient α, as adapted to the present situation. For electric dipole radiation,

$$\alpha = 4/(a_0\kappa)^3ka, \tag{2}$$

where a factor of $\frac{1}{2}$ has been introduced to account for there being only one electron to which energy can be coupled (rather than the two K electrons of the internal conversion problem). Here $a_0 = \hbar^2\epsilon/m_i{}^*e^2$ is the Bohr radius altered to include the dielectric constant ϵ of the crystal and the effective mass $m_i{}^*$ of the electron in its initial state, $a = \hbar^2n^2/m_f{}^*e^2$, where $m_f{}^*$ is the effective mass of the Auger electron, $k \cong [2m_f{}^*\omega/\hbar]^{1/2}$ is the approximate wave number of the Auger electron, and $\kappa = \omega n/c$ is the wave number of the light quantum from the radiative process. Therefore,

$$\alpha = \left(\frac{\sqrt{2}cm_i{}^*}{\epsilon}\right)^3\left(\frac{1}{\hbar\omega}\right)^{7/2}\left(\frac{e^2}{\hbar}\right)^4\frac{m_f{}^{*1/2}}{n^5}. \tag{3}$$

For the exciton bound to the neutral S donor in GaP, $\omega = 3.51\times10^{15}$ rad/sec, $\epsilon = 10.2$, $n = 3.47$, and we estimate $m_i{}^* \approx 0.25m_0$ and $m_f{}^* \approx m_0$. Therefore $\alpha = 1200$, which is in reasonable agreement with the absorption-emission discrepancy figure. Since the assumptions in the derivation of Eq. (2) are not wholly applicable to the problem at hand, this agreement must be regarded as somewhat fortuitous. However, it seems clear from this calculation that the Auger process will predominate over the radiative one in this bound-exciton complex in GaP.

A number of calculations of Auger processes in solids have been made previously. Some have considered three free carriers[9]; some, two free carriers and one bound carrier[10-12]; some, one free carrier and two bound carriers[12-14]; some, three bound carriers[15-17]; and some, one free exciton and one bound carrier.[18] Two of the calculations[15,16] apply to excitons bound to F centers in alkali halides. Khas[17] considered excitons bound to neutral donors or acceptors in semiconductors. His detailed results apply to excitons bound to filled, acceptorlike, Cu-ion vacancies in Cu_2O. He found that the Auger process in this case should be 10^5 times stronger than the radiative process. Since his detailed formulas apply to forbidden direct processes, they are not applicable to GaP.

Other experimental results on GaP support our interpretation. First, it is known that luminescence from either donor-acceptor pairs[19] or excitons bound to isoelectronic traps[20] in GaP can have near unit quantum efficiency at low temperatures and low doping levels. This is possible since the Auger process proposed here cannot occur for either of these luminescence mechanisms. On the other hand, the C-line luminescence, which must compete with the Auger process, is very inefficient. We have measured its quantum efficiency in photoluminescence at 4.2°K in a number of crystals to be one part in 700 ± 200. This agrees with the ratio of the measured decay time of the C line to the calculated radiative lifetime from Eq. (1). Since light of photon energies greater than the band gap energy was used for the quantum efficiency measurements, this agreement also indicates that the Auger process is the dominant recombination process in these crystals at low temperatures. A second source of support for our interpretation comes from the observed ability of the recombination process to couple energy to the remaining electron. This is demonstrated by the observation[21] of radiation on the low-frequency side of the C line which is not simply phonon-assisted C-line emission. A group of weak emission lines are observed which results from bound-exciton recombination with the simultaneous elevation of the second electron to any of several excited states of the S donor. At still lower frequencies a broad, weak continuum of emission is observed corresponding to the excitation of this second electron into the conduction band.

Since these partially radiative processes have no corresponding absorption under normal experimental conditions, their effect on the calculated radiative lifetime was not considered in Eq. (1). We have measured in emission the strength of the discrete lines and the continuum for the first 0.1 eV toward lower energy. If we assume the continuum to then remain at a constant level down to zero frequency, the predicted radiative lifetime of the bound-exciton complex is reduced only by a factor of 2. Though this should be a large overestimate, it is far from explaining the absorption-emission discrepancy of 500.

Clinching proof of the existence of the simple Auger process would come from the detection of the electron ejected into the conduction band. This would be indicated by the observation of the *C* line as a peak in the photoconductivity spectrum at a temperature low enough that thermal ionization of the bound-exciton complex into current carriers would be exceedingly improbable. For such a *C*-line peak to be observable, it must be comparable with background photoconductivity due to valence-band–shallow-donor and acceptor–conduction-band transitions. For the latter processes the defect center which must recapture the free carrier will usually be an uncharged center and thus lead to a substantial lifetime. The Auger electron released subsequent to absorption in the *C* line, on the other hand, will be recaptured by a charged S atom and so have a short lifetime. It thus seems unlikely that a *C*-line photoconductivity peak will be observable at low temperatures. Experiments aimed at its observation at 4.2°K have borne this out. Its previous observation at 77°K[22] is not relevant here since thermal ionization is very important at that temperature.

We have performed measurements on As-doped Si analogous to those reported here for GaP. From absorption measurements on the resonance line belonging to an exciton bound to a neutral As atom, a radiative lifetime of 750 μsec is predicted from Eq. (1). In calculating this we have used $\lambda = 1.078\ \mu$, $n = 3.56$, $g_1 = 2$, and $g_2 = 4$, and have multiplied the integral over the resonance line by 3.2 to account for the ratio of vibronic to electronic transitions in the emission spectrum. The decay time of the resonance-line light was measured to be 0.08 μsec. This yields an absorption-emission discrepancy of 9400 which we interpret as due to the predominance of Auger recombination. The quantum efficiency of the bound-exciton complex was measured to be one part in 4000, in substantial agreement with the lifetime ratio. With $\epsilon = 11.7$, $m_i^* = 0.25 m_0$, and $m_f^* \approx m_0$, Eq. (3) predicts the ratio to be 7900, again in good agreement with experiment and in support of the Auger-recombination interpretation.

We believe that the Auger-recombination mechanism discussed here should predominate in the decay of excitons bound to neutral donors or acceptors for a wide variety of semiconductors, since no use here has been made of properties unique to GaP or to Si.

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MIXING OF VISIBLE AND NEAR-RESONANCE INFRARED LIGHT IN GaP

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Sum and difference frequency generation are observed when visible laser light is mixed in GaP with each of five infrared laser frequencies near the reststrahl. The measured infrared frequency dependence of the nonlinear susceptibility, which varies by a factor of 60, is accounted for by theory.

We have observed radiation at sum and difference frequencies upon mixing infrared and visible laser light in a GaP crystal. The mixing was observed for five different infrared (IR) laser frequencies (211.6, 303.7, 353.7, 357.5, and 428.0 cm^{-1}) lying near the lattice resonance (reststrahl) at 365 cm^{-1}. This enabled us to measure for the first time the variation of the nonlinear susceptibility as the infrared frequency passed through the reststrahl region. By making use of the relationship between spontaneous Raman scattering and frequency mixing, we have been able to account theoretically for the IR frequency dependence of the nonlinear susceptibility.

A Cassegrainian optical arrangement was employed to bring a 6328-Å He-Ne laser beam and the IR beam to a common focus on the surface of a room-temperature GaP crystal. The visible laser produced 150 to 300 mW, and the time-averaged powers in the IR laser lines were approximately 0.17 mW at 211.6 cm^{-1}, 0.43 mW, at 303.7 cm^{-1}, 0.04 mW at 353.7 cm^{-1}, 5.7 mW at 357.5 cm^{-1}, and 1.1 mW at 428.0 cm^{-1}. Both laser beams were limited to narrow cones about the 110 axis. We observed the light scattered in the forward 110 direction with a 2-meter Bausch and Lomb spectrograph, using both photography and gated photon counting (IR-synchronous) to record the intensities. The IR powers were measured with a Golay cell and a thermopile roughly calibrated for 30-μ radiation.

Figure 1(a) shows the dispersion curves for the IR-frequency waves which can propagate in a GaP crystal. Near the lattice resonance, at $\omega_0 = 365\ \mathrm{cm}^{-1}$, the transverse waves have both photon and phonon character. They are known as polaritons.[1] This experiment is an outgrowth of a previous one in which the polariton dispersion curve was plotted out experimentally from ω_0 to 307 cm^{-1} by the observation of spontaneous Raman scattering by polaritons.[2,3] Frequency mixing can be viewed as spontaneous Raman scattering by polaritons, enhanced by increasing the population of some of the polariton modes at the IR frequency. Raman scattering and frequency mixing near the reststrahl involve the same nonlinearity parameters. We shall make use of this when we compute the frequency dependence of the nonlinear susceptibility.

Figure 1(b) is a densitometer trace of a plate showing the spectrum of the light forward scattered along the 110 direction. Peaks A, B, and C are due to spontaneous Raman scattering: A, forward scattering by the LO phonons; B, backward scattering by large wave-vector polaritons, accidentally observed because of crystal surface reflections; C, forward scattering by polaritons. Peak C occurs at the matching frequency where the wave-vector mismatch $\Delta k \equiv |\vec{k}_L - \vec{k}_S - \vec{q}\,| = 0$. Here $\vec{k}_L$, $\vec{k}_S$, and $\vec{q}$ refer to the visible laser wave, the scattered wave, and the polariton, respectively. The peak is broad because the matching frequency changes with the scattering angle θ between $\vec{k}_L$ and $\vec{k}_S$; the collecting optics accepted a cone of scattered light with $0° \leq \theta \leq 0.8°$. The lines labeled by frequencies were present only when the IR laser was operating. The intensities of these lines $I(\omega_S)$ ranged over more