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Temperature dependence of the relative integrated intensities of symmetry-allowed phonon-assisted exciton emission in Si and Ge†

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A model in which we interpret the observed temperature dependence of the relative intensities of symmetry-allowed phonon-assisted exciton emission in Si and Ge is developed. The model is based on a splitting of the exciton ground state combined with different transition rates for the split exciton levels. Symmetry arguments are applied to reduce the relative transition rates for the various phonon-assisted transitions to a minimum number of parameters involving products of reduced matrix elements and energy denominators. If the parameters are determined by comparison with experiment, good quantitative agreement is achieved.

I. INTRODUCTION

In a pure indirect band-gap semiconductor, optical absorption and recombination must be phonon assisted. Of the indirect band-gap semiconductors, the low-temperature optical properties of Si and Ge have probably been the most thoroughly studied. The fundamental absorption edge is characterized by exciton creation. The luminescence spectra have features due to exciton recombination and recombination in the electron-hole liquid (EHL). In Ge, all four phonon-assisted transitions have been observed[1-5]; in Si, TA-, TO-, and LO-phonon-assisted transitions have been observed.[3,6-9] The TO- and LA-phonon-assisted processes are symmetry allowed in Ge, while the LO- and TA-phonon-assisted transitions are forbidden.[10] In Si, all phonon-assisted transitions are symmetry allowed.[10] (The LA-phonon contribution in Si appears to be weak for reasons other than symmetry.)

Recently, a temperature dependence in the ratio of exciton emission intensities for different allowed transitions has been observed in both Si (LO/TO) and Ge (TO/LA).[11,12] In this paper we develop a model in which to interpret this temperature dependence. We will relate the intensity ratio of exciton emission to the corresponding ratios in absorption and EHL emission both of which are independent of temperature in the temperature range we consider (temperatures low enough that the phonons involved in the optical transitions are not thermally excited). The temperature dependence of the intensity ratios for allowed transitions discussed here should be distinguished from the well-understood temperature dependence of the intensity ratio of forbidden to allowed transitions (e.g., TA/LA in Ge).[4,10] The physical origin of these two effects is quite different.

The temperature dependence in the allowed exciton emission intensity ratios can be explained as due to the ground-state splitting of the exciton[13,14] combined with different transition rates for the split exciton levels. The splitting of the exciton ground state is much smaller than the energy differences of the various phonons. In Si, the lines due to the split exciton ground state have not been resolved in either emission or absorption. In Ge, the splitting of the exciton ground state is larger than in Si and transitions to the two levels have been clearly resolved in absorption.[5,15-17] Thermal broadening of the exciton lines prevent a complete separation in emission; luminescence from the weakly bound exciton state appears as a slight shoulder in the spectrum.[18,19] Therefore, with the exception of high-resolution absorption experiments in Ge, the experimental emission and absorption spectra consist of essentially unresolved transitions from both exciton levels. The relative probabilities of occupying the two levels depend on temperature. If the transition rates for the two levels are different, the integrated luminescence intensity from each phonon-assisted transition (which includes emission from both exciton levels) will depend on temperature.

To understand the temperature dependence of the exciton intensity ratios, it is necessary to know the ratios of transition rates for the two exciton levels via the various phonon-assisted processes. Information about these transition rates can be attained from symmetry. After symmetry has been taken into account, a small number of parameters, involving ratios of reduced matrix elements of the electron-phonon interaction Hamiltonian, remain to be determined by comparison with experiment. The purpose of this paper is to describe in detail the model used to interpret the temperature dependence of the exciton emission intensity ratios in Si and Ge and to apply symmetry arguments to reduce the ratios of the various transition rates to a small number of parameters involving reduced ma-

trix elements of the electron-phonon interaction Hamiltonian.

The paper is organized as follows: The basic model is discussed in Sec. II, symmetry arguments are applied to gain information about the transition rates in Sec. III, in Sec. IV, we summarize our results.

II. MODEL

In Si and Ge, the 1s exciton ground state is split into two fourfold-degenerate levels.[13,14] (In counting degeneracy, we have included electron spin and restricted our attention to one of the conduction-band minima.) Physically, this splitting can be viewed as due to a perturbation of the fourfold-degenerate hole states at the top of the valence band by the axial charge density of the electron. The electron charge density is axial in the exciton bound state because of the axial anisotropy of the electron kinetic energy. The optical transition matrix elements between the four $k=0$ hole states and a conduction band minimum state is different for each hole state. The transition rates for the two split exciton levels depend on the amplitudes for the hole states to be included in that level. In this section we derive expressions for the exciton emission and absorption rates and the EHL emission rate in terms of one electron transition matrix elements.

The exciton wave function can be described using the perturbation approach developed by Baldereschi and Lipari.[14,20] In this approach, the exciton effective-mass Hamiltonian is divided into a "s-like" piece and a smaller "d-like" piece. The "d-like" piece of the Hamiltonian is treated as a perturbation. The unperturbed ground-state wave functions are[21]

$$\psi_{\alpha,\sigma,K}=e^{i\vec{K}\cdot(\beta_e\vec{r}_e+\beta_h\vec{r}_h)}\Theta_{1s}(r_e-r_h)\theta_\sigma(r_e)\phi_\alpha(r_h)\,, \tag{1}$$

where θ_σ and ϕ_α are the periodic part of the electron and hole Bloch functions, Θ_{1s} is a 1s hydrogenic function, σ refers to electron spin and conduction-band minimum, and α runs over the four degenerate $k=0$ hole states. The "center of mass" motion of the exciton is described by the wave vector K (referred to the conduction-band minimum) and the effective-mass parameters β_e and β_h come from a center-of-mass transformation of the "s-like" piece of the Hamiltonian. (They are explicitly defined in Ref. 21, but since they do not play an important role in our considerations, we won't repeat the definition here.) The "d-like" perturbation splits the degenerate states of the unperturbed Hamiltonian into two levels. We approximate the exciton wave functions by the linear combinations of zeroth-order wave functions which diagonalize the effective Hamiltonian of degenerate second-order perturbation theory,

$$\Psi_{\lambda\sigma K}=\sum_\alpha \chi_{\lambda\alpha}(K)\psi_{\alpha\sigma K}\,. \tag{2}$$

Here $\chi_{\lambda\alpha}$ is a 4×4 unitary matrix which depends on the exciton wave vector.

The integrated intensity ratio for different phonon-assisted processes is equal to the ratio of relative transition rates to emit a photon of any energy. Neglecting the wave-vector dependence of the one-electron matrix elements, the relative transition rates for an exciton to recombine by emitting a photon of an energy and a phonon of type η is easily seen to be

$$R_\eta=\sum_{\lambda\sigma K}\left|\sum_\alpha \chi_{\lambda\alpha}(K)M_{\alpha\sigma\eta}\right|^2 e^{-E_\lambda(K)/k_BT}\,, \tag{3a}$$

where

$$M_{\alpha\sigma\eta}=\sum_I\left(\frac{\langle\phi_\alpha|\hat{\xi}\cdot\vec{\mathrm{P}}|I\rangle\langle I|H_{ep}^\eta|\theta_\sigma\rangle}{\epsilon_c-\epsilon_I}+\frac{\langle\phi_\alpha|H_{ep}^\eta|I\rangle\langle I|\hat{\xi}\cdot\vec{\mathrm{P}}|\theta_\sigma\rangle}{\epsilon_v-\epsilon_I}\right). \tag{3b}$$

Here $E_\lambda(K)$ is the exciton energy, P is the one-electron momentum operator, $\hat{\xi}$ is the photon polarization vector, H_{ep}^η is the η phonon piece of the electron-phonon interaction Hamiltonian, and ϵ is a one-electron energy. We have neglected the phonon energy compared with electronic energies. In Eq. (3a), sums over photon polarization (and phonon polarization for the transverse modes) have not been explicitly written. We have dropped factors which are common to all phonon transitions in the relative rates, since they will cancel in the integrated intensity ratios.

The absorption spectrum for the various symmetry-allowed phonon-assisted transitions are somewhat different and the relative rate for absorbing a photon depends on the photon energy. Measuring the photon energy from the threshold for absorption by each phonon-assisted process (ω_η) and assuming the incident photon beam is unpolarized, the relative absorption rates are

$$A_\eta(\omega-\omega_\eta)=\sum_{\lambda\sigma K}\left|\sum_\alpha \chi_{\lambda\alpha}(K)M_{\alpha\sigma\eta}\right|^2 \times F(\omega-\omega_\eta-E_\lambda(K))\,, \tag{4}$$

where F is a broadening function which includes lifetime and instrumental broadening. If the width of the broadening function is greater than the splitting between the exciton levels, transitions to the two exciton levels are not resolved. In this case,

the absorption spectrum for each phonon-assisted transition can be reasonably approximated by a square-root line shape. The ratio of the absorption rates can be defined as the intensity ratio of these square-root line shapes.

The relative transition rate for an electron and a hole in an EHL to recombine by emitting a photon of any energy and a phonon of type η is

$$D_\eta = \sum_{\alpha\alpha'\sigma} M_{\alpha\sigma\eta} M^*_{\alpha'\sigma\eta} \sum_{k_h b} B_{b\alpha}(\hat{k}_h) B^*_{b\alpha'}(\hat{k}_h) \sum_{k_e} \mathrm{Tr}(e^{-H/k_B T} C^\dagger_{\sigma k_e} C^\dagger_{b k_h} C_{b k_h} C_{\sigma k_e}) , \tag{5a}$$

where k_e, k_h, and b are electron and hole wave vectors and the hole band index, respectively; H is the Hamiltonian describing the EHL, C is a carrier annihilation operator, and $B_{b\alpha}$ is given by

$$B_{b\alpha}(\hat{k}_h) = \lim_{|\vec{k}_h| \to 0} \langle U_{b\vec{k}_h} | \phi_\alpha \rangle . \tag{5b}$$

Here $U_{b\vec{k}_h}$ is the periodic piece of the Bloch function for band b and wave vector $\vec{k}_h$. For fixed band index, the four matrix elements $B_{b\alpha}(k_h)$ transform into each other like the Γ_8^+ irreducible representation of O_h. If we can neglect correlations between the hole wave vector and the conduction-band minimum (σ) which appears in the trace of Eq. (5a), this trace just gives the probability that the hole state labeled by $(b, \vec{k}_h)$ is occupied in the droplet. Considered as a function of $\vec{k}_h$, it transforms like the identity representation of O_h. Therefore, we have

$$\sum_{k_h} B_{b\alpha}(\hat{k}_h) B^*_{b\alpha'}(k_h) \sum_{k_e} \mathrm{Tr}(e^{-H/k_B T} C^\dagger_{\sigma k_e} C^\dagger_{b k_h} C_{b k_h} C_{\sigma k_e}) = \langle (\Gamma_8^+)_{\alpha'} | \Gamma_1 | (\Gamma_8^+)_\alpha \rangle = \delta_{\alpha\alpha'} G , \tag{6}$$

where G is independent of α. Neglecting factors which are common to all phonon assisted transitions, the relative transition rates for EHL are

$$D_\eta = \sum_{\alpha\sigma} |M_{\alpha\sigma\eta}|^2 . \tag{7}$$

The expressions for the relative transition rates are complicated because of the wave-vector dependence of χ and the complicated exciton dispersion relations.[21] We expect that the detailed wave vector dependence of χ and E will be largely smoothed out when the wave-vector integral is performed. We are interested in temperatures such that $k_B T$ is much less than the exciton binding energy; therefore, we are interested in the small-K behavior of χ and E_λ. As $|K|$ goes to zero, χ (and, of course, E_λ) approaches a definite limit which does not depend on the angle of $\vec{K}$. For $|K|$ small, deviations in χ from its $K=0$ value will tend to oscillate to zero in the angular wave-vector integral. We approximate χ by its value at zero wave vector. In addition, we neglect differences in the exciton dispersion relation between the two exciton states in the small wave-vector regime. These differences in the dispersion relations cause differences in the density of states for the two exciton levels of about 5% for Si,[21] and about 30% for Ge.[17] Neglecting factors which are common to all phonon assisted transitions, the relative transition rates for exciton emission is approximated by

$$R_\eta = \sum_{\lambda\sigma} \left| \sum_\alpha \chi_{\lambda\alpha}(0) M_{\alpha\sigma\eta} \right|^2 e^{-E_\lambda(0)/k_B T} . \tag{8}$$

In absorption, we assume that the broadening is large compared to the splitting between the exciton states and approximate the relative absorption rates by

$$A_\eta = \sum_{\lambda\sigma} \left| \sum_\alpha \chi_{\lambda\alpha}(0) M_{\alpha\sigma\eta} \right|^2 = D_\eta . \tag{9}$$

We have used the fact that χ is a unitary matrix.

The simplified approximate expressions for the relative transition rates [Eqs. (8) and (9)] predict that the EHL emission ratios and the absorption ratios are equal to each other and to the high-temperature limit of exciton emission ratios. In Si, the LO/TO absorption ratio has been shown experimentally to equal the high-temperature limit of the exciton emission ratio[11]; and in Ge, the TO/LA EHL emission ratio has been shown experimentally to equal the high-temperature limit of the exciton emission ratio.[12] The LO/TO EHL emission ratio cannot be measured in Si because the width of the EHL line is greater than the separation of these phonon energies. The TO/LA absorption ratio is difficult to measure in Ge because the weak TO absorption lies on a large background due to the strong LA absorption.

The basic point of this model is that the weighting of the one-electron matrix elements $M_{\alpha\sigma\eta}$ changes with temperature in exciton emission. This change in weighting is due to the fact that the four $k=0$ hole states are occupied with different probability in the two exciton levels. As the temperature is changed, the relative probability of occupying the two levels change. In EHL emission, the four hole states are occupied with equal probability and the one electron matrix elements are equally weighted. In absorption, the one-electron matrix elements are also weighted equally.

III. SYMMETRY CONSIDERATIONS

The parameters $M_{\alpha\sigma\eta}$ which appear in the expressions for the relative transition rates involve matrix elements of the electron-phonon interaction for short-wavelength phonons. It is difficult to compute such matrix elements. However, symmetry arguments can be used to reduce the number of parameters which appear in the relative transition rates. In effect, we compute Clebsch-Gordan coefficients and take the reduced matrix elements to be parameters to be determined by comparison with experiment. We construct basis functions for the hole states in the exciton treating the spin-orbit interaction and exciton splitting as successively smaller perturbations. We then compute Clebsch-Gordan coefficients for the spatial part of the matrix elements. This procedure is preferable to working in the double group, because it allows us to drop reduced matrix elements which we know to be small on physical grounds (due, for example, to coupling of different bands by the spin-orbit interaction). We use the notation of Bouckaert, Smoluchowski, and Wigner[22] when referring to irreducible representations of the single point groups and that of Elliott[23] for irreducible representations of the double groups.

The transition matrix elements in Si and Ge involve zone-center valence-band Bloch functions. The symmetry group at the zone center is O_h. The valence-band Bloch functions at the zone center are made up of spatial functions which transform like the Γ'_{25} representation of O_h combined with a spinor. We will use a representation of Γ'_{25} defined by the basis functions (YZ, XZ, XY), where the X, Y, and Z axes are along [100] crystallographic directions. The spin-orbit interaction splits the sixfold-degenerate hole states into fourfold-degenerate and twofold-degenerate sets of states. The fourfold-degenerate set of states, which transforms like the Γ_8^+ representation of the O_h double group, is at the top of the valence band. For symmetry purposes, the states at the top of the valence band can be written

$$\phi_{3/2} = (1/\sqrt{2})(YZ + iXZ)\uparrow , \tag{10a}$$

$$\phi_{-3/2} = T\phi_{3/2} , \tag{10b}$$

$$\phi_{1/2} = [2/(6)^{1/2}]XY\uparrow - [1/(6)^{1/2}](YZ + iXZ)\downarrow , \tag{10c}$$

$$\phi_{-1/2} = T\phi_{1/2} , \tag{10d}$$

where T is the time-reversal operator and $\uparrow$ is a spinor quantized along the Z direction.[24]

The states ϕ_α are not mixed in forming the exciton in Si; that is, $\chi_{\lambda\alpha}(0)$ is the identity matrix. The states $\alpha = \pm\frac{3}{2}$ are in the more tightly bound (Δ_6) exciton and the states $\alpha = \pm\frac{1}{2}$ are in the less tightly bound (Δ_7) exciton.

The conduction-band minima in Si occur along ⟨100⟩ directions. We will concentrate on one particular conduction-band minimum which we take to lie along the Z axis. The symmetry of the conduction-band state is Δ_1. There is no spin-orbit splitting of the electron states at the conduction-band minimum.

The optical transition matrix can involve phonon scattering of either the electron or the hole. The important scattering processes in Si, illustrated in Fig. 1, are: an electron in the state Δ_1 emits a phonon and makes a transition to the Γ_{15} state or the somewhat higher-energy Γ'_2 state at the zone center; it then recombines with a hole in the Δ_6 or Δ_7 state emitting a photon.[25] A hole in the Δ_6 or Δ_7 state emits a phonon and makes a transition to the Δ_5 state; it then recombines with the electron in the state Δ_1. We neglect transitions through other intermediate states because of the large energy denominators that would be involved. We also neglect spin-orbit coupling in the intermediate states.

We first consider conduction-band scattering through the Γ_{15} intermediate state. To describe the phonon-scattering process, we must work in the group C_{4v}. The electron state at the conduction-band minimum transforms like the identity representation Δ_1. The Γ_{15} representation of O_h is

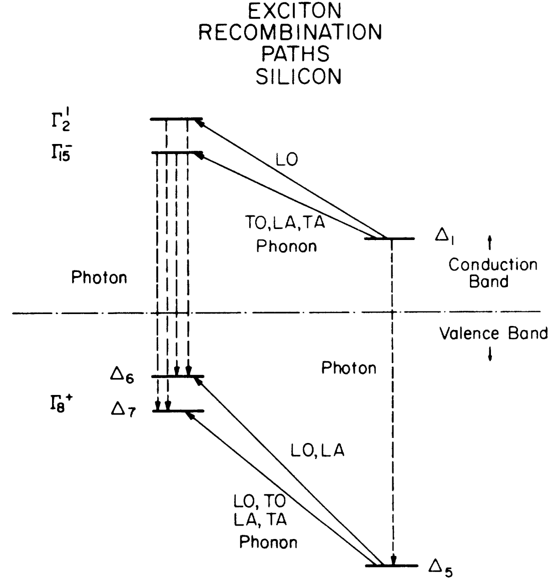

FIG. 1. Schematic diagram of the recombination processes in silicon. The splitting of the ground state of the exciton is shown in the hole band where the fourfold-degeneracy of the Γ_8^+ states is split into two twofold-degenerate states Δ_6 and Δ_7 which are labeled according to the irreducible representations of the group of $\vec{K}$ for $\vec{K}$ along the Δ direction.

compatible with the Δ_5 and Δ_1 representations of C_{4v}.[22] We have

$$\Delta_1 \times \Delta_1 = \Delta_1 \,, \tag{11a}$$

$$\Delta_1 \times \Delta_5 = \Delta_5 \,. \tag{11b}$$

Therefore, TA and TO phonons, which transform like Δ_5, and LA phonons, which transform like Δ_1, can participate in the scattering. The LO phonon, which transforms like Δ_2', is forbidden. We take the representation of Δ_5 defined by the basis functions (X, Y) where Z is the symmetry axis. The Clebsch-Gordan coefficients for C_{4v} with this representation of Δ_5 are tabulated in Ref. 26.

The zone-center photon matrix element can be described in the group O_h. The photon transforms like Γ_{15} and the spatial part of the hole wave function transforms like Γ_{25}'. Since we have

$$\Gamma_{15} \times \Gamma_{25}' = \Gamma_2' + \Gamma_{12}' + \Gamma_{25} + \Gamma_{15} \,, \tag{12}$$

the transition is allowed. We take the representation for Γ_{15} defined by the basis functions (X, Y, Z); the Clebsch-Gordan coefficients are tabulated in Ref. 26. The product of matrix elements can be written in terms of reduced matrix as

$$\sum_{I \in \Gamma_{15}} \langle \phi_\alpha | \hat{\zeta} \cdot \vec{P} | I \rangle \langle I | H_{ep}^{\eta} | \theta_\sigma \rangle = C_{(\alpha, \sigma, \hat{\zeta})} \langle \phi \| P \| \Gamma_{15} \rangle \langle \Gamma_{15} \| H_{ep}^{\eta} \| \theta \rangle \,. \tag{13}$$

The numerical coefficients are tabulated in Table I.

Only LO-phonon scattering through the Γ_2' intermediate state is allowed. The numerical coefficients, defined in analogy with Eq. (13), are included in Table I.

The discussion of hole scattering is very similar to that for electron scattering. The numerical coefficients, defined in analogy with Eq. (13), are tabulated in Table II.

Performing the summations indicated in Eq. (8), the relative exciton emission rates are given by

$$R_T = \tfrac{1}{2} |W_T|^2 + \left(\tfrac{1}{6} |W_T|^2 + \tfrac{4}{6} |W_T + Q_T|^2\right) e^{-\Delta E / k_B T} \,, \tag{14a}$$

$$R_{\rm LO} = \tfrac{1}{2} |Q_{\rm LO} + S_{\rm LO}|^2 + \left(\tfrac{1}{6} |Q_{\rm LO} + S_{\rm LO}|^2 + \tfrac{1}{3} |S_{\rm LO}|^2\right) e^{-\Delta E / k_B T} \,, \tag{14b}$$

$$R_{\rm LA} = \tfrac{1}{2} |Q_{\rm LA} + W_{\rm LA}|^2 + \tfrac{1}{6} |Q_{\rm LA} + W_{\rm LA}|^2 e^{-\Delta E / k_B T} \,, \tag{14c}$$

$$W_\eta = \langle \phi \| P \| \Gamma_{15} \rangle \langle \Gamma_{15} \| H_{ep}^{\eta} \| \theta \rangle / \Delta E_c \,, \tag{14d}$$

$$S_\eta = (2/\sqrt{3}) \langle \phi \| P \| \Gamma_2' \rangle \langle \Gamma_2' \| H_{ep}^{\eta} \| \theta \rangle / \Delta E_c' \,, \tag{14e}$$

$$Q_\eta = \langle \phi \| H_{ep}^{\eta} \| \Delta_5 \rangle \langle \Delta_5 \| P \| \theta \rangle / \Delta E_v \,. \tag{14f}$$

The subscript T in Eq. (14a) refers to both transverse modes; ΔE_c, $\Delta E_c'$, and ΔE_v refer to the energy denominators for conduction-band scattering through the Γ_{15} intermediate state, the Γ_2' intermediate state and valence-band scattering, respectively.

Scattering of the electron through the conduction band and the hole through the valence band can interfere and information about the relative phases of the parameters W_η, Q_η, and S_η is useful. The Si crystal has inversion symmetry. The conjugation operator can be defined as the product of the inversion operator and the time-reversal operator. Both the momentum operator and the electron-phonon interaction Hamiltonian commute with the conjugation operator; therefore, the matrix elements with eigenstates of the one-electron Hamiltonian can be chosen real.[27] The ratios W_η / Q_η and S_η / Q_η must, therefore, be real.

TABLE I. Numerical coefficients for conduction-band scattering in Si; states are labeled (α, σ) where α refers to the hole state and σ refers to the electron spin; T_x refers to a transverse phonon (either TA or TO) of X polarization. Coefficients referring to LO-phonon scattering are for the Γ_2' intermediate state; coefficients for the other phonons are for the Γ_{15} intermediate state.

Photon polarization	X	Y	Z
$\frac{3}{2}\uparrow$	$(i/2\sqrt{2})$(LA)$[-1/(6)^{1/2}]$(LO)	$(-1/2\sqrt{2})$(LA)$[i/(6)^{1/2}]$(LO)	$(i/2\sqrt{2})(T_x)(-1/2\sqrt{2})(T_y)$
$\frac{3}{2}\downarrow$	0	0	0
$-\frac{3}{2}\uparrow$	0	0	0
$-\frac{3}{2}\downarrow$	$(-i/2\sqrt{2})$(LA)$[-1/(6)^{1/2}]$(LO)	$(-1/2\sqrt{2})$(LA)$[-i/(6)^{1/2}]$(LO)	$(-i/2\sqrt{2})(T_x)(-1/2\sqrt{2})(T_y)$
$\frac{1}{2}\uparrow$	$[1/(6)^{1/2}](T_y)$	$[1/(6)^{1/2}](T_x)$	$(2/3\sqrt{2})$(LO)
$\frac{1}{2}\downarrow$	$[i/2(6)^{1/2}]$(LA)$(-1/3\sqrt{2})$(LO)	$[-1/2(6)^{1/2}]$(LA)$(i/3\sqrt{2})$(LO)	$[i/2(6)^{1/2}](T_x)[-1/2(6)^{1/2}](T_y)$
$-\frac{1}{2}\uparrow$	$[i/2(6)^{1/2}]$(LA)$(1/3\sqrt{2})$(LO)	$[1/2(6)^{1/2}]$(LA)$(i/3\sqrt{2})$(LO)	$[i/2(6)^{1/2}](T_x)[1/2(6)^{1/2}](T_y)$
$-\frac{1}{2}\downarrow$	$[1/(6)^{1/2}](T_y)$	$[1/(6)^{1/2}](T_x)$	$(2/3\sqrt{2})$(LO)

TABLE II. Numerical coefficients for valence band scattering in Si; states are labeled (α,σ) where α refers to the hole state and σ refers to the electron spin; T_x refers to a transverse phonon (either Ta or TO) of X polarization.

Photon polarization	X	Y	Z
$\frac{3}{2}\uparrow$	$(-1/2\sqrt{2})$(LO)$(i/2\sqrt{2})$(LA)	$(i/2\sqrt{2})$(LO)$(-1/2\sqrt{2})$(LA)	0
$\frac{3}{2}\downarrow$	0	0	0
$-\frac{3}{2}\uparrow$	0	0	0
$-\frac{3}{2}\downarrow$	$(-1/2\sqrt{2})$(LO)$(-1/2\sqrt{2})$(LA)	$(-i/2\sqrt{2})$(LO)$(-1/2\sqrt{2})$(LA)	0
$\frac{1}{2}\uparrow$	$[1/(6)^{1/2}](T_y)$	$[1/(6)^{1/2}](T_x)$	0
$\frac{1}{2}\downarrow$	$[-1/2(6)^{1/2}]$(LO)$[-1/2(6)^{1/2}]$(LA)	$[i/2(6)^{1/2}]$(LO)$[-1/2(6)^{1/2}]$(LA)	0
$-\frac{1}{2}\uparrow$	$[1/2(6)^{1/2}]$(LO)$[i/2(6)^{1/2}]$(LA)	$[i/2(6)^{1/2}]$(LO)$[1/2(6)^{1/2}]$(LA)	0
$-\frac{1}{2}\downarrow$	$[1/(6)^{1/2}](T_y)$	$[1/(6)^{1/2}](T_x)$	0

The exciton intensity ratios for emission via the various phonon-assisted processes are given by the ratios of relative exciton emission rates. The rather large temperature dependence of the LO/TO intensity ratio in Si can be accounted for if electron scattering and hole scattering interfere constructively. (These are the strong phonon-assisted transitions in Si.) In this case, the LO-phonon-assisted transition rate is larger in the tightly bound Δ_6 exciton than it is in the weakly bound Δ_7 exciton, but the TO-phonon-assisted transition rate is larger in the weakly bound Δ_7 exciton than in the tightly bound Δ_6 exciton. As the temperature is raised and the probability that the exciton is in the tightly bound state decreases from unity at zero temperature to one-half at high temperature; the LO-assisted transition rate increases. Therefore the LO/TO intensity ratio decreases with increasing temperature. If we estimate $W_{\mathrm{TO}} \sim Q_{\mathrm{TO}}$ and $Q_{\mathrm{LO}} \sim S_{\mathrm{LO}}$ (the relevant energy denominators are comparable), the predicted drop in the LO/TO intensity ratio from $T \ll \Delta E$ to $T \gg \Delta E$ is about a factor of 4. Experimentally, the LO/TO intensity ratio in Si drops by about a factor of 3 from $T = 2.1$ to 13 K ($\Delta E \sim 5$ °K).[11] Of course, the quantitative behavior of the intensity ratios depends on the details of the reduced matrix elements; the above estimate simply shows that the qualitative behavior of the intensity ratio can be accounted for with reasonable estimates of these parameters.

The relative transition rates can be directly measured in a stress experiment. If a small uniaxial stress is applied along the [100] direction, the four hole states at the top of the valence-band split in the same manner as in the exciton in unstressed material [same $\chi_{\lambda\alpha}(0)$].[28] With stress, the size of the splitting can be increased so that transitions to the two hole levels can be easily resolved. In addition, the electron valley in the [100] direction is lowered in energy compared with the [010] and [001] valleys. As a result, transitions from the electron in the [100] valley to the two split hole levels can be clearly resolved and their relative strengths can be determined. These are the same transitions which occur in the split exciton in unstressed material. This experiment has been performed for the TO-phonon-assisted transition.[29] After summing over photon polarizations, the TO-phonon-assisted transition rate in the weakly bound Δ_7 exciton was found to be about seven times larger than for the tightly bound Δ_6 exciton.[29,30] This result is in reasonable agreement with our estimate of this ratio (setting $W_{\mathrm{TO}} \sim Q_{\mathrm{TO}}$ suggests this ratio should be about six), supports the belief that electron and hole scattering interfere constructively in the TO-phonon transition (the alternative possibility is that $|Q_{\mathrm{TO}}|$ is several times larger than $|W_{\mathrm{TO}}|$), and strongly confirms our basic model.

Calculations of the numerical coefficients, defined in analogy with Eq. (13), in Ge are very similar to that of Si. We briefly discuss the differences in the two cases and give the final results for Ge. The functions ϕ_α may be represented by Eq. (10) as in Si. However, because the position of the conduction-band minima are different in Ge than in Si, the states ϕ_α are mixed in the exciton in Ge; that is, $\chi_{\lambda\alpha}(0)$ is not the identity matrix in Ge. We first diagonalize the exciton effective Hamiltonian of degenerate second-order perturbation theory to determine $\chi_{\lambda\alpha}(0)$. The spatial part of the hole state in the more tightly bound $(L_4^+ + L_5^+)$ exciton transforms like L_3 and the spatial part of the less tightly bound (L_6^+) exciton has pieces which transform like both L_1 and L_3. The important intermediate states for electron scattering transform like Γ_2' and for hole scattering like L_3'. In

both scattering paths, the parity of the wave function is changed so that only odd phonon- (LA and TO) assisted transitions are allowed.[10] Computing the numerical coefficients as in the case of Si, the relative exciton emission rates are found to be

$$R_{\rm TO} = |Q_{\rm TO}|^2 + |Q_{\rm TO}|^2(\tfrac{1}{3} + \tfrac{2}{3}|V|^2)e^{-\Delta E/k_B T}, \quad (15a)$$

$$R_{\rm LA} = \tfrac{1}{2}|Q_{\rm LA} + W_{\rm LA}|^2 + (\tfrac{1}{3}|W_{\rm LA}|^2 + \tfrac{1}{6}|Q_{\rm LA} + W_{\rm LA}|^2)e^{-\Delta E/k_B T}, \quad (15b)$$

$$V = \langle \phi; L_1 \| H_{ep}^{\rm TO} \| L_3' \rangle / \langle \phi; L_3 \| H_{ep}^{\rm TO} \| L_3' \rangle, \quad (15c)$$

$$W_\eta = (2/\sqrt{3}) \langle \phi; \Gamma_{25}' \| P \| \Gamma_2' \rangle \langle \Gamma_2' \| H_{ep}^{\eta} \| \theta \rangle / \Delta E_c, \quad (15d)$$

$$Q_\eta = \langle \phi; L_3 \| H_{ep}^{\eta} \| L_3' \rangle \langle L_3' \| P \| \theta \rangle / \Delta E_v. \quad (15e)$$

Here $|\phi; \Gamma_{25}'\rangle$, $|\phi; L_3\rangle$, and $|\phi; L_1\rangle$ refer to the spatial part of the hole wave function which transforms like the Γ_{25}' representation of O_h and linear combinations of these functions which transform like the L_3 and L_1 representations of the group D_{3d}, respectively. As in Si, the ratio W_η/Q_η is real.

The TO/LA exciton emission intensity ratio has been observed in Ge.[12] In Ge, LA-phonon conduction-band scattering should be much more important than LA-phonon valence-band scattering because the energy denominator is much smaller for conduction-band scattering ($\Delta E_c \ll \Delta E_v$ in Ge, in Si $\Delta E_c \lesssim \Delta E_v$). We drop $Q_{\rm LA}$ compared with $W_{\rm LA}$. The normalized LA-phonon-assisted transition rate is then approximately independent of temperature. The TO/LA intensity ratio will depend on the parameter $|V|$. We would guess that $|V|$ is of order unity; this estimate predicts that the TO/LA exciton emission intensity ratio is independent of temperature in Ge. In fact, the TO/LA intensity ratio in Ge decreases by about[12] 15% (compared with a factor of 3 decrease of the LO/TO intensity ratio in Si). This small decrease can be accounted for if $|V| < 1$. If one estimates $|V|^2$ by constructing basis functions of the representation L_3' from a linear combination of the basis functions of Γ_{15} (in the tight-binding approximation, the L_3' states are constructed this way), the result is $|V|^2 = \frac{1}{2}$.

IV. SUMMARY AND DISCUSSION

We have presented a model in which we interpret the observed temperature dependence of the relative intensities of symmetry-allowed phonon-assisted exciton emission in Si and Ge. The model is based on a splitting of the exciton ground state combined with different transition rates for the split exciton levels. A simplified, approximate form of the general model is developed. The simplified form of the model predicts that the electron-hole droplet emission ratios and the absorption ratios are equal to each other and to the high-temperature limit of the exciton emission ratios. These qualitative predictions are in agreement with experimental observations.[11,12] Symmetry arguments have been applied to reduce the matrix elements which appear in the model to a small number of parameters involving products of reduced matrix elements and energy denominators. The qualitative behavior of the intensity ratios (e.g., the LO/TO ratio in Si decreases with temperature and the temperature dependence is large, whereas, the temperature dependence of the TO/LA ratio in Ge is much smaller) follows from symmetry and reasonable estimates of the parameters. The detailed behavior of the intensity ratios depends on the exact values of the reduced matrix elements. If the reduced matrix elements are determined by comparison with experiment, good quantitative agreement is achieved.[11,12] The value of the exciton splitting required to fit the experimental LO/TO ratio data in[11] Si ($0.3 \leq \Delta E \leq 0.7$ meV) is close to the theoretical value.[13,14] In Ge, the exciton splitting has been measured directly,[5,15-17] and the experimental value can be used to get a good fit of the TO/LA ratio data.[12] Because the simplified version of the model is in reasonable agreement with experiment, we have not returned to the more detailed form.

In discussing the exciton emission intensity ratios, we have concentrated on Si and Ge because the temperature dependence of the intensity ratios has been experimentally observed in these materials. However, a similar effect should occur in any indirect band gap semiconductor.

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[28]It is clearly essential that the stress be applied in a [100] direction in Si; if the stress were applied in some other direction (say [111]) the splitting of the hole states would be quite different than that which occurs in the exciton in unstressed material [i.e., $\chi_{\lambda\alpha}(0)$ would be completely different in the two cases]. As a result the relative transition rates observed in such an experiment would not be related in any simple sense to those which appear in the split exciton in unstressed material. In Ge, the stress should be applied in the [111] direction.

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