Temperature Dependence of Silicon Luminescence Due to Splitting of the Indirect Ground State*

R. B. Hammond, D. L. Smith, and T. C. McGill†
California Institute of Technology, Pasadena, California 91125
(Received 28 July 1975)

The temperature dependence of the ratio of LO- to TO-phonon-assisted recombination luminescence of the indirect exciton in silicon is reported. The ratio is found to differ from that observed in absorption and to vary from ~0.3 at 2°K to ~0.1 at 13°K. The variation of the ratio with temperature is shown to be due to the splitting of the ground state of the exciton by several tenths of a meV. The relevance of these results to the recombination from the electron-hole condensate in silicon is discussed.

The emission and absorption of radiation due to indirect excitons in silicon at low temperatures has been the subject of a number of investigations.[1-5] Features identified with TA-, LO-, and TO-phonon-assisted transitions have been identified. Dean, Yafet, and Haynes,[3] Shaklee and Nahory,[4] and Nishino, Takeda, and Hamakawa[5] have studied the absorption at temperatures less than 10°K. Shaklee and Nahory[4] have correctly interpreted the two features at approximately 1.22 eV as due to absorption with the emission of a LO or TO phonon. These two lines are split by approximately 2 meV. Dean, Yafet, and Haynes[3] have investigated the recombination spectrum at 2.5 and 5.5°K. They observed two lines at approximately 1.10 eV which they attributed to valley-orbit splitting of the exciton state. Further, they found that the ratio of the relative intensities of these two lines varied with temperature in such a way as to suggest that thermal equilibrium was not established between the two states. Shaklee and Nahory[4] have pointed out that valley-orbit splitting should not occur and that the *two* lines observed in luminescence are in fact due to *two* processes involving the LO and TO phonon, respectively. While this interpretation indicates the origin of the lines, it does not suggest why the ratio of the LO- to TO-phonon process in emission, γ_E, should show the temperature dependence hinted at by the data of Ref. 3 at two temperatures.

In this Letter, we report on a systematic investigation of the temperature dependence of the recombination processes via LO- and TO-phonon emission. We find that the ratio γ_E varies with temperature in agreement with the two experimental points given by Ref. 3. This variation of γ is shown to come from the fact that the observed LO and TO recombination lines are each made up of two unresolved lines from two exciton states split by less than 1 meV. The splitting of the ground state of the exciton into twofold degenerate states, Δ_6 and Δ_7, is due to the interaction of the hole at $\vec{K}=0$ with the anisotropic charge density of the electron in the conduction band.[6,7] These two states are found to possess different relative rates for TO- and LO-phonon emission in recombination. Hence, a temperature-dependent variation of the relative occupancy of these two exciton states leads to a temperature dependence in γ_E. Analysis of the experimental data gives an energy splitting between the Δ_6 and Δ_7 states in qualitative agreement with the theoretical values given by McLean and Loudon[6] and Lipari and Baldereschi.[7] Although this splitting has been explored in detail theoretically, we believe this is the first experimental observation of the consequences of this splitting in silicon.

The emission spectrum from a sample of laser-excited silicon is shown in Fig. 1. The silicon crystal was high-purity p type with a net impurity concentration $N_A - N_D \sim 2\times10^{11}$ cm^{-3}. The spectrum was obtained by illuminating the sample with a GaAs laser which produced pulses of 2 μsec duration with a repetition rate of 20 kHz. The optical power was approximately 3 W. The luminescence was analyzed with a Spex 1400-II spectrometer, detected with an RCA 7102 S-1 photomultiplier tube operated at 195°K, and processed with a lock-in amplifier. The spectrum was independent of laser power and hence showed no evidence of heating.

The luminescence line shape was fitted with the expression proposed by Elliott.[8] The intensity was assumed to vary as

$$I(E) \sim (E - E_x)^{1/2} \exp[-(E - E_x)/k_B T], \qquad (1)$$

where E_x is the threshold energy. This theoretical expression for the intensity was modified to include the effects of detector sensitivity, spec-

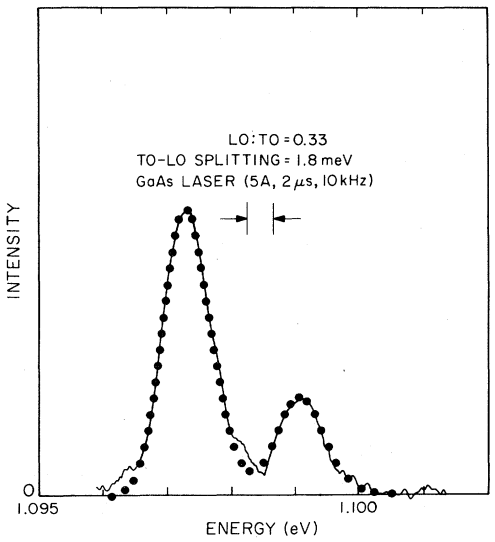

FIG. 1. Luminescence spectrum of silicon at 2.1°K. The silicon was excited using a GaAs laser. The solid line shows the experimental results. The TO-assisted recombination produces the line centered at ~1.097 eV. The LO-assisted recombination produces the line centered at ~1.099 eV. The dots are the theoretical line shape produced by the procudure described in the text.

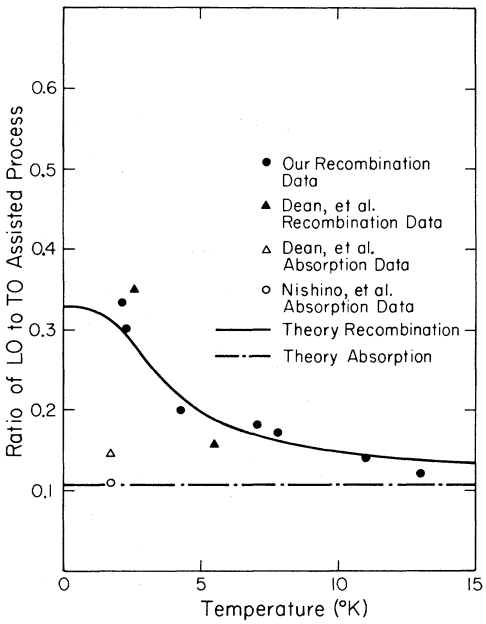

FIG. 2. The ratio of LO- to TO-phonon-assisted emission and absorption as a function of temperature. The experimental data shown by ▲ and △ are from Ref. 3; those shown by ○, from Ref. 5. The theoretical curves are obtained by taking $\Delta E = 0.6$ MeV and, with A positive, $A = 2.2$ and $B = 1.3$, or with A negative, $A = -0.4$ and $B = 0.2$. Both of these sets of values produce identical curves.

trometer transmission and broadening, and a Gaussian broadening due to phonon lifetime.

The theoretical curve in Fig. 1 was obtained using this procedure with energy broadening due to phonon lifetime characterized by a standard deviation of 0.34 meV; an energy separation between the TO and LO lines of 1.8 meV; a temperature of 2.1°K, the bath temperature; and γ_E of 0.33. The value of the broadening used here is in agreement with the value deduced from derivative absorption spectroscopy.[5]

Spectra at other temperatures exhibit similar features except that as temperature is increased the separated lines tend to merge. The values of γ_E at other temperatures were obtained by the same line-fitting procedure. The results of these experiments along with the results reported by other authors for emission and absorption[3,5] are given in Fig. 2. These results show that γ_E varies from ~0.3 at 2.1°K to ~0.1 at 13°K. The data also show that γ_E approaches the ratio for absorption γ_A at higher temperatures.

The variation of γ_E with temperature may be understood in terms of the splitting of the ground-state exciton level into two levels separated by an energy ΔE. The ratio $\gamma_E(T)$ is given by

$$\gamma_E(T) = \frac{R_{LO}{}^{\Delta_6} + R_{LO}{}^{\Delta_7} \exp(-\Delta E/k_B T)}{R_{TO}{}^{\Delta_6} + R_{TO}{}^{\Delta_7} \exp(-\Delta E/k_B T)}, \qquad (2)$$

where $R_{LO}{}^{\Delta_6}$ and $R_{LO}{}^{\Delta_7}$ are the rates for photon emission via LO-phonon emission for the more tightly bound state Δ_6 and the split-off excited state derived from the ground state Δ_7, respectively. $R_{TO}{}^{\Delta_6}$ and $R_{TO}{}^{\Delta_7}$ are defined in an analogous way for the TO-phonon-assisted process. In absorption the ratio γ_A is given by the ratio of the sum of the rates. For high temperatures such that $k_B T \gg \Delta E$, we have that $\gamma_E(T)$ approaches γ_A in agreement with experiment.

From Eq. (2) it is clear that to predict $\gamma_E(T)$, we must know the ratios of the various rates. As illustrated in Fig. 3, the two most likely recombination paths are as follows: (1) The electron emits a phonon and makes a transition from the Δ_1 state in the conduction band to the Γ_{15}^- state in the conduction band and then recombines with a hole in either the Δ_6 state in the case of the more tightly bound exciton or the Δ_7 state in the case of the less tightly bound exciton. The process is allowed for TO-phonon emission only.[9] (2) The electron in Δ_5 emits a phonon and recombines with a hole in the state Δ_6 or Δ_7, respectively. Then the electron in state Δ_1 in the con-

duction band recombines with the hole in Δ_5, emitting a photon. When the hole is in the Δ_6 state, this process is allowed for the LO phonon only, and is TO- and LO-phonon allowed when the hole is in the Δ_7 state. A group-theoretical study of the relative rates[10,11] using an analysis similar to that used by Lax and Hopfield[9] leads us to conclude that $\gamma_E(T)$ must be of the form

$$\gamma_E(T) = |B|^2 \left[\frac{3+\exp(-\Delta E/k_B T)}{3|A|^2+[4|A+1|^2+|A|^2]\exp(-\Delta E/k_B T)}\right], \tag{3}$$

where A and B involve ratios of energy denominators from the second-order perturbation theory, the reduced matrix elements[12] of the momentum operator p, and the TO and LO part of the electron-phonon interaction Hamiltonian H_{ep}^{TO} and H_{ep}^{LO}, respectively:

$$A = \left(\frac{\Delta E_v}{\Delta E_c}\right)\left(\frac{\langle \Gamma_{25}^+ \| p \| \Gamma_{15}^- \rangle \langle \Gamma_{15}^- \| H_{ep}^{\mathrm{TO}} \| \Delta_1 \rangle}{\langle \Delta_5 \| p \| \Delta_1 \rangle \langle \Gamma_{25}^+ \| H_{ep}^{\mathrm{TO}} \| \Delta_5 \rangle}\right), \tag{4}$$

where ΔE_v and ΔE_c are the energy denominators for transitions through the Δ_5 and Γ_{15}^- states, respectively; and

$$B = \frac{\langle \Gamma_{25}^+ \| H_{ep}^{\mathrm{LO}} \| \Delta_5 \rangle}{\langle \Gamma_{25}^+ \| H_{ep}^{\mathrm{TO}} \| \Delta_5 \rangle}. \tag{5}$$

Since the space group for the diamond lattice contains the inversion symmetry and the states must be invariant under time reversal, then A and B may be taken to be real.[13] The sign of B is irrelevant in Eq. (3) but the sign of A is important. The exact values of A and B cannot be obtained from our analysis but we expect A and B to be of order unity. Regardless of the values of A and B, Eq. (3) shows that γ_E must decrease with increasing temperature.

The comparison between the experimental results and theoretical results for both emission and absorption is contained in Fig. 2. The values of ΔE, A, and B were determined by a least-squares fit to the experimental data, excluding that obtained from Dean, Yafet, and Haynes.[3] The value of ΔE which produced the best fit is 0.6 meV. The values of A and B are not uniquely determined by this procedure; either $A=2.2$ and $B=1.3$ or $A=-0.4$ and $B=0.2$ produce the same curve. The theoretical curves for γ_E and γ_A for these parameters are shown in the figure. The agreement between the experimental results and theoretical calculations is quite good. The value of ΔE taken here is in good agreement with the calculations of McLean and Loudon.[6] However, the agreement is not greatly changed for a range of values of ΔE between 0.3 and 0.7 meV. While we are unable to give a precise value for the splitting, the good agreement between theory and experiment provides the first experimental confirmation of the splitting of the ground state of the exciton in silicon.

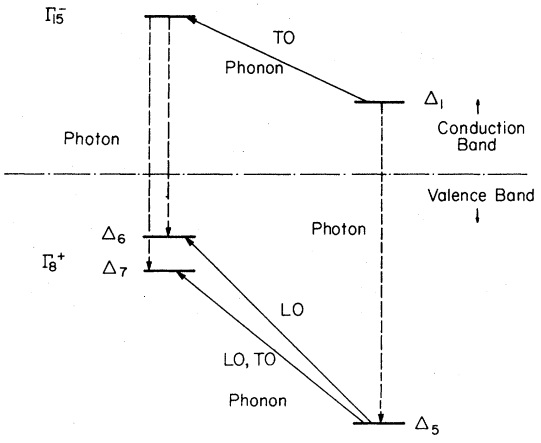

FIG. 3. Schematic diagram of the two recombination processes in silicon. The splitting of the ground state of the exciton is shown in the hole band where the fourfold degeneracy of the Γ_8^+ states is split into the two twofold degenerate states Δ_6 and Δ_7 which are labeled according to the irreducible representations of the group of $\vec{K}$ for $\vec{K}$ along the Δ direction.

The luminescence from the electron-hole condensate in silicon also possesses a strong line due to LO- and TO-phonon-assisted recombination.[14-16] In this case it is not possible to resolve the two lines since the intrinsic width of the condensate line, approximately 12 meV, is greater than the splitting between the TO- and LO-assisted lines. However, in fitting the condensate line shape, it is essential to have a value for the ratio of these two processes.[16] Since holes in the condensate should occupy the states Δ_6 and Δ_7 with equal probability, the correct value of the ratio of LO to TO processes is the value observed in exciton absorption, $\gamma=0.11$.

The authors gratefully acknowledge an essential discussion with J. J. Hopfield and many useful discussions with J. W. Mayer.

*Work supported in part by the U. S. Office of Naval Research under Contract No. N00014-67-A-0094-0036 and the U. S. Air Force Office of Scientific Research under Grant No. 73-2490.

†Alfred P. Sloan Foundation Fellow.

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COMMENTS

Fine-Structure Corrections and Electromagnetic Decays of Charmonium*

J. Pumplin, W. Repko, and A. Sato†

Department of Physics, Michigan State University, East Lansing, Michigan 48824

(Received 4 August 1975)

We calculate fine-structure corrections to the spectrum of ψ/J particles in the charmonium model, assuming that the linear potential which confines the quarks is due to an effective vector exchange. We also calculate the electromagnetic decay rates between the various low-lying s and p states.

Recent observations of monoenergetic γ rays in colliding-beam experiments at DESY[1] and at Stanford Linear Accelerator Center[2] lend support to the charmonium model[3] of the narrow resonances $\psi(3.1)$ and $\psi(3.7)$. In particular, the prediction[4,5] of three p states, with masses around 3.5 GeV, and the associated γ-ray decay schemes, could form a basis for understanding the data. A measurement of the spacing between the $^3P_0$, $^3P_1$, and $^3P_2$ levels—assuming they are found—will yield information about the quark-antiquark ($c\bar{c}$) dynamics. Therefore, we have calculated these fine-structure splittings, under the assumption that the two-body system is essentially nonrelativistic[3] and that the binding results from an effective vector exchange which provides quark confinement.

Specifically, we assume an effective $c\bar{c}$ interaction in momentum space of the form

$$I=(\gamma_4\gamma_\mu)^{(1)}(\gamma_4\gamma_\mu)^{(2)}\bar{v}(k^2), \tag{1}$$

where k is the four-momentum transfer and $\bar{v}(k^2)$ is a confining potential. In the nonrelativistic limit, where $k_0 \to 0$, the Fourier transform of $\bar{v}(\vec{k}^2)$ is $v(r)$, the potential used in the two-body Schrödinger equation. To obtain the lowest-order relativistic corrections to $v(r)$, we expand Eq. (1) to order $(v/c)^2$ and express the result in nonrelativistic (two-component) form. We then transform to coordinate space