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Valley-Orbit Splitting of the Indirect Free Exciton in Silicon

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Fine structure has been observed in the indirect edge absorption and luminescence spectra of hyperpure silicon. It is shown that this structure is due to a splitting in the energy states of the free indirect exciton rather than to transitions involving additional phonons. Two free-exciton states are observed, separated by 1.8±0.2 meV. The intensity ratio of the two luminescence components associated with these exciton states indicates that thermal equilibrium is achieved between them at ~5.5°K but not at ~2.5°K. This fact, together with the magnitude of the splitting, suggests that these two states do not arise from spin-spin interaction in the free exciton or from a splitting of the degenerate hole states because of coupling to the anisotropic electrons at Δ_1. Instead, these experimental results, together with the intensity ratio of the two free-exciton absorption components, indicate that the splitting occurs because the binding energy of the 1s envelope state of the free exciton is significantly larger (~11.5 meV) when it contains a symmetric linear combination of conduction-band states; i.e., the observed splitting is due to the valley-orbit interaction. A further weakly bound free-exciton state observed in absorption is attributed to an excited envelope state.

I. INTRODUCTION

The absorption edge spectra of silicon and germanium were the first to be analyzed according to the detailed theory of indirect transitions which includes the effects of electron-hole interactions (excitons) as well as interactions with lattice vibrations (phonons).[1] Phonon interactions are necessary for momentum conservation in optical absorption or emission (luminescence) at an indirect gap in a defect-free semiconductor. Processes involving phonon emission are predominant at the lowest temperatures. For such processes, Elliott has shown[2] that the indirect absorption coefficient α should vary with photon energy $h\nu$ according to

$$\alpha_i(h\nu)=a(T)(h\nu-E_{gx}-\hbar\omega_i)^{1/2}, \qquad (1)$$

where $a(T)$ is a weakly temperature-dependent parameter containing the density-of-states effective masses of electrons and holes, E_{gx} is the exciton energy gap, and $\hbar\omega_i$ is the energy of the ith momentum-conserving phonon. Absorption due to the phonon-assisted creation of free-electron–hole pairs commences at energy E_x above each exciton absorption component, where E_x is the internal binding energy of the free exciton. The free pair absorption is predicted to have the form

$$\alpha_i(h\nu)=b(T)B(h\nu-E_{gx}-E_x-\hbar\omega_i). \qquad (2)$$

For energies above the thresholds $E_{0i}=E_{gx}+E_x+\hbar\omega_i$ comparable with E_x, the function $B(h\nu)$ has the form $(h\nu-E_{gx}-E_x-\hbar\omega_i)^{3/2}$. Function $b(T)$ has properties similar to $a(T)$ in Eq. (1).

MacFarlane, McLean, Quarrington, and Roberts[1] (hereafter abbreviated MMQR) analyzed the low-temperature absorption edge of silicon according to Eqs. (1) and (2). They identified two phonon-assisted transitions involving an 18.3- and a 57.8-meV phonon. These phonons are derived from the transverse acoustical (TA) and transverse optical (TO) branches of the lattice vibrational spectrum of silicon,[3] and their magnitudes, together with other considerations,[4] serve to identify the positions of the conduction-band minima within the Brillouin zone. The valence-band maxima are at the center of the zone, symmetry classification Γ_{25}, while the six equivalent conduction-band minima are at (0.82,0,0), symmetry classification Δ_1. MMQR claimed that the absorption associated with each phonon-assisted transition followed Eq. (1) for the first 5.5 meV above threshold, when a second component of similar form was observed. This component was associated with an excited state of the free exciton, which was estimated to have a binding energy of ~10 meV. Haynes *et al.*[5] showed that the shapes of luminescence bands due to the recombination of free excitons in silicon at 18 and 83°K are consistent with expectation from the absorption data of MMQR according to a detailed balance calculation.

In the present paper, attention is restricted to a detailed examination of the emission and low-level absorption spectra measured at helium temperatures. The free-exciton luminescence was found to contain two prominent components, 1 and 2, separated by ~1.8 meV. The lower-energy component 1, unanticipated from the absorption analysis of MMQR, is prominent because of thermal quenching of the luminescence from the upper component, indicating a splitting in the excited state of the transition. The relatively weak absorption component corresponding to luminescence component (1) can be clearly seen in the new absorption edge spectra obtained with improved spectral resolution, but can also be discerned in the original data of MMQR.[6] The form of these components

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* Deceased.

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is consistent with free-exciton transitions. It is suggested that the small energy difference between these exciton states arises from an increase in the binding energy of free excitons derived from a symmetric combination of conduction-band states, i.e.,; it is due to the valley-orbit interaction. A higher-lying free-exciton transition is observed in absorption, probably due to an excited orbital state of the free exciton.

II. EXPERIMENTAL

The techniques necessary to obtain well-resolved spectra of the weak near band-gap luminescence of silicon have been discussed elsewhere.[7] In the present work, all measurements were made with the silicon single crystals immersed in liquid helium which was sometimes pumped below the λ point. For the luminescence studies, crystals ~10 mm×5 mm×1 mm were cut from vacuum-floating-zone-refined single-crystal ingots of silicon with room-temperature resistivities $\gtrsim 9000\ \Omega$ cm, obtained from several different manufacturers. The crystals were etched with CP8 and treated in steam for 20 min before mounting in the Dewar to minimize surface recombination. The exciting light from a 200-W mercury arc filtered by a 1-cm water cell and two 0.5-cm Jena KG1 filters was focused onto a surface of the crystal. The luminescence was detected from the opposite surface by a Perkin Elmer Model 112 spectrometer equipped with a 1200-line/mm grating and a cooled lead sulphide photodetector. The infrared radiation was chopped at 25 cps, and the signal was detected using standard lock-in techniques and displayed on a chart recorder.

Transmission measurements were made on single crystals of cross section 7 mm×3 mm and lengths in the range 5–16 mm. The polished end faces of one crystal 16.5 mm long were shaped and partially aluminized so that the light made three passes within the crystal before emerging to the spectrometer. A tungsten-iodine lamp was used as source, and the visible radiation was removed with a gallium arsenide filter. The absorption spectra were calculated from transmission spectra using the method discussed by Dean and Thomas.[8] Below the intrinsic absorption edge, the spectral dependence of the light transmitted by the refined silicon crystals was identical to the spectral variation of the light intensity recorded in the absence of the crystal. Weak absorption commencing at the free-exciton energy gap E_{gx} was observed in some Czochralski-grown carbon-doped polycrystalline samples.

III. RESULTS

A. Low-Temperature Absorption Edge Spectrum

The knees in the low-temperature absorption edge of refined silicon are clearly evident in Fig. 1. There are two principal sets of absorption thresholds, involving indirect transitions, respectively, associated with the emission of TA or TO momentum-conserving phonons. The magnitude of the absorption indicated in Fig. 1 is in good agreement with that measured by MMQR,[1,6] except for the effects of a weak absorption tail evident in the MMQR data near the threshold of the TA-phonon-assisted components. A plausible source of this absorption tail is no-phonon indirect transitions due to residual carbon in the crystals by MMQR. Such transitions are possible, since electron momentum may be conserved in the indirect transition by scattering in the local field of the impurity ions.[9] Doped crystals containing ~5×10^{17}-cm^{-3} substitutional carbon impurities according to the strength of the localized lattice vibrational mode due to carbon[10] exhibit a no-phonon absorption edge component 10% as strong

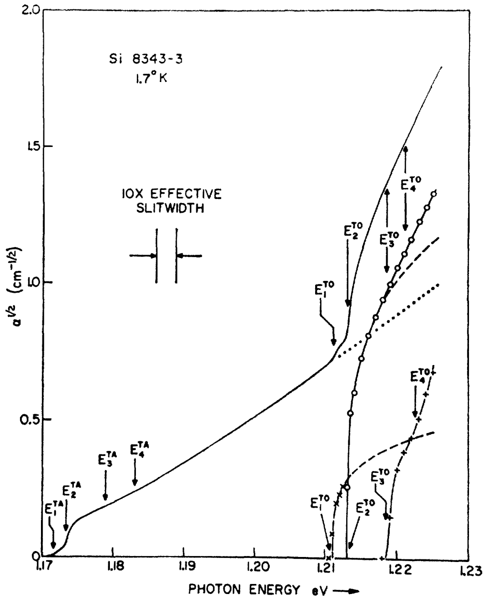

FIG. 1. Low-level absorption edge spectrum of refined silicon at 1.7°K. The absorption data were obtained from transmission measurements on a 0.52-cm-thick single crystal (above 1.205 eV), a 1.65-cm crystal (1.195–1.215 eV) and a triple pass in the 1.65-cm crystal (below 1.2 eV). The vertical arrows denote thresholds of absorption components discussed in the text. The absorption due to TO-phonon-assisted transitions has been analyzed into its components after subtraction of the extrapolated absorption due to TA-phonon-assisted transitions (dotted line). Points x represent the free-exciton component with threshold at E_1^{TO} thus revealed. Points o were obtained after subtraction of a MB fit (dashed line) to points x. Points + were obtained after further subtraction of a MB fit to the initial portion of the o curve, and represent absorption due to the creation of excitons in excited orbital states and to the creation of unbound electron-hole pairs above E_4^{TO}.

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as that due to TA-phonon-assisted transitions in an undoped crystal. Thus, the absoprtion at E_1^{TA} due to these no-phonon transitions is ~0.014 cm^{-1} for 5×10^{17}-cm^{-3} carbon impurities. MMQR report an absorption tail of ~0.001 cm^{-1} at this energy, which implies ~4×10^{16}-cm^{-3} carbon in their crystals. It is reasonable to suggest such a level of carbon contamination in silicon crystals available in early 1958. The no-phonon free-exciton component due to carbon in silicon can be sensitively detected in emission.[11] Its absence in the vacuum-floating-zone-refined crystals used in the present measurements implies that this material contains $\lesssim 10^{16}$-cm^{-3} substitutional carbon atoms.[12]

The structure in Fig. 1 is more clearly defined than that obtained by MMQR, probably because more highly refined single crystals of silicon were used in the present work. The individual absorption components in the experimental spectra deviate slightly from the theoretical forms in Eqs. (1) and (2). This effect is most readily seen as a broadening of the low-energy thresholds of the experimental free-exciton components, which then rise less rapidly than $(h\nu-E_0)^{1/2}$. MMQR have shown that this broadening increases rapidly with temperature above ~50°K and attribute this to a lifetime effect arising from the inelastic scattering of free excitons by phonons. Below ~50°K MMQR observed a temperature-independent broadening consistent with a relaxation time of ~3.4×10^{-12} sec for inelastic scattering of free excitons by lattice imperfections and by spontaneously emitted phonons. The decreased broadening in Fig. 1 suggests that imperfection scattering was indeed more significant in the crystals used by MMQR, consistent with the appearance of an absorption tail in the MMQR data. The Gaussian broadening parameter for the experimental free-exciton absorption components in Fig. 1 is ~0.3 meV, which implies that the low-temperature relaxation time against inelastic scattering is ~1.4×10^{-11} sec in the 10^3 Ω-cm crystals used in the present work. This is still much shorter than the relaxation times for electrons in refined silicon at 2°K derived from cyclotron resonance linewidths[13] (~1.5×10^{-9} sec). It is even slightly shorter than the relaxation times derived from the mobilities of *p*- and *n*-type silicon at 20°K [14] (~2.2×10^{-11} sec), and there is good reason to believe that these conductivity relaxation times will increase considerably below 20°K. It may be that the exciton relaxation time cannot be reliably estimated from the broadening of the absorption and emission (Sec. III A) components because of contributions from small unresolved splittings of the exciton states due to effects discussed in Sec. IV.

Two components can be clearly seen near the threshold of the TO-phonon-assisted free-exciton transitions in the absorption edge spectra obtained in the present work. The thresholds of these components are labeled E_1^{TO} and E_2^{TO} in Fig. 1. The relatively weak lower-energy component can also be seen in the original absorption data obtained by MMQR,[6] but its shape was less clearly defined owing to the greater relaxation broadening in their crystals. Component E_1^{TO} was neglected in the analysis reported by MMQR.[1] This component might be attributed to the creation of free excitons with the emission of longitudinal optical (LO) momentum-conserving phonons. However, the observed energy separation $E_2^{\mathrm{TO}}-E_1^{\mathrm{TO}}$ is slightly less than 2 meV, whereas the energy difference between TO and LO phonons of wave vector close to that selected by momentum conservation is known to be >3 meV.[15]

The presence of a pair of TA-phonon-assisted absorption components with a similar threshold separation (Fig. 1) provides additional confirmation that these pairs of components arise from an electronic energy splitting rather than from contributions associated with other branches of the lattice vibrational spectrum of silicon. This viewpoint is further strengthened by the observation of thermalization in the intensity ratio of the corresponding luminescence components (Sec. III B). Traces of the extremely weak absorption component E_1^{TA} can also be seen in the absorption data of MMQR.[6]

Figure 1 shows that the absorption rises above both E_1^{TO} and E_2^{TO} as $(h\nu-E_0)^{1/2}$, which indicates that both components involve the creation of free excitons. Neglecting relaxation broadening, the TO-phonon-assisted interband absorption can be represented by the basic form

$$\alpha h\nu = 2.25(h\nu-E_1^{\mathrm{TO}})^{1/2}+15.2(h\nu-E_1^{\mathrm{TO}}-0.002)^{1/2} +\beta(h\nu-E_1^{\mathrm{TO}}-0.0075), \quad (3)$$

where α is measured in cm^{-1} and the energy is in eV. The function β was found by MMQR to commence as $(\Delta E)^{1/2}$ as expected for the creation of free excitons [Eq. (1)], then to rise as $(\Delta E)^{3/2}$ after ~4.5 meV because of the onset of transitions to free-electron–hole pair states. The present results are consistent with this behavior. Threshold energies for the free-electron–hole pair absorption components are labeled E_4^{TA} and E_4^{TO} in Fig. 1. Like MMQR,[1] we assume that the $(\Delta E)^{1/2}$ behavior near the thresholds of function β (E_3^{TA} and E_3^{TO} in Fig. 1) is due to an excited orbital state of the free exciton. The TA-phonon-assisted interband absorption can likewise be represented by the basic form

$$\alpha h\nu = 0.06(h\nu-E_1^{\mathrm{TA}})^{1/2}+0.445(h\nu-E_1^{\mathrm{TA}}-0.002)^{1/2} +0.068\beta(h\nu-E_1^{\mathrm{TA}}-0.0075). \quad (4)$$

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TABLE I. Analysis of the threshold energies of some intrinsic absorption and emission components in silicon.

Component	Threshold Energy (eV)	Identification	Analysis[a]
(a) E_1^{TA}	1.1717 ± 0.0003	$E_{gx1}+\hbar\omega_{\mathrm{TA}}$	$\Delta E_{x12}=1.8$, 2.0, and 1.8 meV from (b)–(a), (f)–(e), and (j)–(i)
(b) E_2^{TA}	1.1735 ± 0.0002	$E_{gx2}+\hbar\omega_{\mathrm{TA}}$	
(c) E_3^{TA}	$1.179\ \pm0.0003$	$E_{gx3}+\hbar\omega_{\mathrm{TA}}$	$\Delta E_{x13}=7.3$ and 7.5 meV from (c)–(a) and (g)–(e)
(d) E_4^{TA}	$1.183\ \pm0.0005$	$E_g+\hbar\omega_{\mathrm{TA}}$	
(e) E_1^{TO}	1.2110 ± 0.0002	$E_{gx1}+\hbar\omega_{\mathrm{TO}}$	$E_{x1}=11.5\pm0.8$ meV from (d)–(a) and (h)–(e)
(f) E_2^{TO}	1.2130 ± 0.0002	$E_{gx2}+\hbar\omega_{\mathrm{TO}}$	$E_{x2}=9.5\pm0.5$ meV from (d)–(b) and (h)–(f)
(g) E_3^{TO}	$1.2185+0.0003$	$E_{gx3}+\hbar\omega_{\mathrm{TO}}$	$E_{gx1}=1.1533\pm0.0003$ eV and $E_{gx2}=1.1552\pm0.003$ eV from (e)–(i) and (f)–(j),
(h) E_4^{TO}	1.2225 ± 0.0005	$E_g+\hbar\omega_{\mathrm{TO}}$	also $\hbar\omega_{\mathrm{TO}}=57.8\pm0.2$ meV
(i) I_1^{TO}	1.0956 ± 0.0001	$E_{gx1}-\hbar\omega_{\mathrm{TO}}$	$E_{gx1}=1.1533\pm0.0004$ eV, $E_{gx2}=1.1551\pm0.0003$ eV from (a) and (b) if
(j) I_2^{TO}	1.0974 ± 0.0001	$E_{gx2}-\hbar\omega_{\mathrm{TO}}$	$\hbar\omega_{\mathrm{TA}}=18.4\pm0.1$ meV[b]
			$E_g=1.1645\pm0.0006$ eV from (d) and (e)

[a] E_{xn} is the internal binding energy of the *n*th resolved state of the free exciton; ΔE_{xmn} is the difference in binding energy of the *m*th and *n*th states. E_{gx1} and E_{gx2} are the two lowest indirect exciton energy gaps, and E_g is the indirect energy gap.

[b] Reference 11.

The threshold energies of the eight absorption components resolved in Fig. 1 are listed in Table I. Energies E_2^{TA} and E_2^{TA} are, respectively, in excellent agreement with E_{1e} and E_{2e} reported by MMQR,[6] if the latter energies are reduced by ~0.5 meV to correct for their use of air spectral calibration wavelengths with a wavelength-to-photon energy conversion factor appropriate to vacuum wavelengths.

The low-temperature indirect energy gap E_g of silicon and the binding energies of the exciton states resolved in the present work, together with the exciton energy gaps, are also shown in Table I. The two excitons of higher binding energy are both believed to be derived from the ground orbital exciton state (Sec. IV). Haynes *et al.*[5] estimated $E_x \sim 8$ meV from an analysis of the shape of the TO-phonon-assisted intrinsic luminescence band at 83°K. According to the absorption forms in Eqs. (3) and (4), detailed balance requires that free-exciton luminescence at 83°K should be predominantly from the states with thresholds at E_2^{TA} and E_2^{TO}.

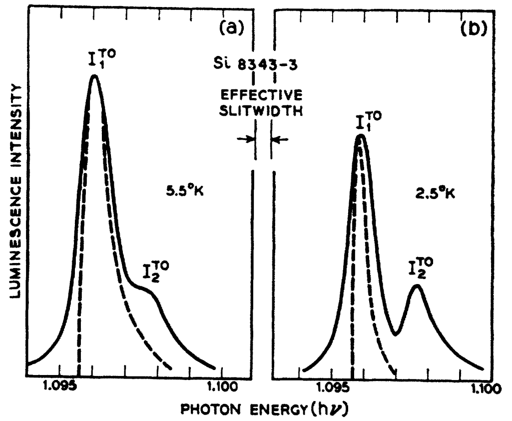

FIG. 2. High-resolution recording of a section of the low-temperature photoluminescence spectrum of a refined-silicon single crystal. Only the portion of the spectrum associated with the TO-phonon-assisted recombination of free excitons is shown. The dashed curves represent MB forms for the indicated temperatures. Possible sources of additional broadening of the experimental lines are discussed in the text.

B. Low-Temperature Free-Exciton Recombination Radiation

Like the intrinsic interband absorption discussed in Sec. III A, the principal band in the luminescence spectrum due to the recombination of free excitons at low temperatures is associated with the *emission* of TO phonons. The low-energy threshold of this band therefore appears at an energy $2\hbar\omega_{\mathrm{TO}}$ below the corresponding absorption threshold. Figure 2 shows two well-resolved subcomponents in the TO-phonon-assisted luminescence of free excitons at helium temperatures. The 2.5°K spectrum was recorded with the helium pumped below the λ point to ~1.9°K according to vapor pressure thermometry, whereas the 5.5°K spectrum was recorded with the helium bath boiling at atmospheric pressure. The temperature of the crystal, which is increased due to irradiation by the ~1.5-W exciting light beam, was roughly estimated from the widths of the spectral lines. For this purpose, the lifetime broadening due to relaxation effects of unresolved splittings of the free exciton (Sec. III A) was assumed to produce a Gaussian broadening parameter of ~0.3 meV in the absence of other sources of broadening, i.e., a full width at half-height of ~0.7 meV. The spectral slitwidth used for Fig. 2 was 0.56 meV. The Maxwell-Boltzmann (MB) distributions shown in Fig. 2 represent the main luminescence components after these two sources of line broadening have been subtracted. The temperatures calculated from these MB distributions are slightly lower than temperatures directly recorded with a carbon resistance thermometer immersed in the helium bath and irradiated by the arc lamp under similar conditions. This difference probably occurred since the carbon resistor absorbed a greater fraction of the incident light because of its lower reflectivity compared with etched silicon.

The energy separation ΔE between the two components I_1^{TO} and I_2^{TO} shown in Fig. 2 is 1.8 ± 0.2 meV, i.e., it is equal to the splittings observed in the free-exciton absorption spectrum (Sec. III A). Using the experimental techniques described in Sec. II, it was not possible to measure the band due to TA-phonon-assisted recombinations with resolution adequate to observe a splitting of this magnitude. Nevertheless, such a splitting is expected to occur according to the interpretation in Sec. IV. The luminescence due to the recombination of single free excitons is weak in silicon at helium temperatures. The dominant intrinsic luminescence is contained in relatively broad bands, not shown in Fig. 2, caused by the decay of excitonic molecules.[16]

Table I shows that the exciton energy gaps and TO-phonon energies derived from these absorption and luminescence studies are mutually consistent. These energy gaps are also consistent with those obtained from the TA-phonon-assisted absorption thresholds obtained from Fig. 1, if the accurate value of the phonon energy $\hbar\omega_{\text{TA}}$ obtained from Ref. 11 is used. The free-carrier indirect energy gap E_g given in Table I is in good agreement with a recent estimate obtained from an analysis of the shape of low-temperature donor-acceptor pair spectra in silicon[17] ($E_g=1.166\pm0.001$ meV).

The change with temperature in the intensity ratio $I_2^{\text{TO}}/I_1^{\text{TO}}$ of the luminescence components shown in Fig. 2 is of considerable interest. At 5.5°K the measured ratio is ~0.16, close to the value 0.13 anticipated from the ratio of the strengths of the corresponding absorption components [~7 according to Eq. (3)], if it is assumed that the populations of these two free-exciton states are in thermal equilibrium at 5.5°K. However, the measured ratio *increases* with decreasing temperature, reaching ~0.35 at 2.5°K. Thus, thermal equilibrium between these exciton states is not achieved at the lowest temperatures. This effect is discussed further in Sec. IV.

Previous detailed measurements of the free-exciton luminescence of silicon were made at much higher temperatures, 18°K or above[5] and 26°K,[11] where the emission is predominantly due to the I_2^{TO} component. For $\Delta E=1.9$ meV, the calculated intensity ratio $I_2^{\text{TO}}/I_1^{\text{TO}}$ is 2.0 at 18°K and ~3.0 at 26°K, assuming thermal equilibrium. The MB threshold deduced for the 18°K spectrum in Ref. 5 is near 1.097 eV, *i.e.*, closest to the threshold of component I_2^{TO} in Fig. 2 (see Table I also) as expected from the above calculation. The half-height bandwidth of the MB distribution is ~$1.5\Delta E$ at 18°K. The experimental spectrum is broadened still further by other effects, so the two subcomponents cannot be clearly resolved at this temperature. Neglect of the contribution of I_1^{TO} to the 18°K spectrum means that the broadening has been considerably overestimated in Ref. 5. Following MMQR, this broadening was attributed to relaxation processes in Ref. 5.

IV. DISCUSSION

The ~1.9-meV splitting in the indirect exciton in silicon might arise from several different effects. The first possibility is spin-spin interaction between the electron and hole. If the relevant electron wave function is derived from the singlet valley-orbit state,[18] the situation would be comparable to that for shallow bound excitons in gallium phosphide.[19] However, the observed splitting is rather larger than would be anticipated for this effect in the weakly bound free-exciton state in silicon.

McLean and Loudon have calculated the internal binding energy of the two lowest states of the indirect exciton in silicon in the effective-mass approximation, using a variational procedure.[20] For a negative value of the valence-band effective-mass parameter L-M, now known to be appropriate,[21] the theoretical results are $13.2\rightarrow13.7$ meV and $12.4\rightarrow13.0$ meV, according to whether the spin-orbit splitting in the valence band is assumed infinite or zero. Thus, the calculated splitting is only about $\frac{1}{3}$ of that shown in Table I, although the theoretical values of E_{gx} are larger than the experimental values. This makes it seem unlikely that the observed splitting is connected with the mechanism considered by McLean and Loudon, which involves a splitting of the hole states owing to the interaction with electrons associated with multiple ellipsoidal conduction-band minima.

A further difficulty with the spin-spin interaction model for the experimental splitting is connected with the lack of thermal equilibrium between these states observed at the lowest temperatures. The lifetime of free excitons in silicon has been measured recently[22] and is ~2 μsec at ~5°K. It follows that the two lowest-energy free-exciton states will be in mutual thermal equilibrium unless the process responsible for the transitions between these states has a characteristic time $>10^{-6}$ sec. If the two exciton states simply involve different total spin quantum numbers, the interexcited-

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[22] J. D. Cuthbert (private communication). This measured lifetime is ~30 times shorter than the value calculated in Ref. 5 from the strength of the intrinsic absorption at 83°K. This discrepancy will increase at 5°K, because the prominence of transitions from the lowest exciton state E_{x1}, which has a smaller absorption cross section [Eqs. (3) and (4)], will substantially increase the calculated lifetime of the free exciton at low temperatures. In fact, it appears that the measured free-exciton lifetimes in silicon are $\lesssim1\%$ of the calculated values at 80°K {V. S. Vavilov and E. L. Nolle, Fiz. i Tekh. Poluprov. **2**, 742 (1968) [English transl.: Soviet Phys.—Semicond. **2**, 616 (1968)]} as well as at 5°K. This discrepancy is consistent with the quantum efficiency of the luminescence, which implies that the measured lifetimes are governed by nonradiative recombination processes.

state transition rate will be governed by the spin-lattice relaxation time of the hole, which is much smaller than for the electron.[23] This process need involve only a single phonon whose momentum can be taken up by the free exciton. At temperatures such that $kT \ll \Delta E$, phonon emission will predominate. The characteristic time for this transition can be calculated, and it is $\sim 10^{-9}$ sec independent of temperature in this range (say, below ~5°K). This is much less than the luminescence decay time, so thermal equilibrium is predicted on this model even at the lowest temperatures, in disagreement with experiment (Fig. 2).

The possibility that the two low-energy exciton states represent the $n=1$ and $n=2$ orbital states of the exciton can be immediately discarded, since the absorption at the higher-energy state is nearly ten times stronger than at the lower state, whereas absorption to the $n=2$ exciton state is expected to be only ~12% of that to the $n=1$ state.[2] In addition, the observed splitting ΔE is much smaller than anticipated for the $n=1 \rightarrow n=2$ energy separation according to the values of E_x given in Table I. The relative strength of the component with threshold at E_3^{TO} (Fig. 1) is slightly larger than this prediction for an $n=2$ state, but it probably contains unresolved contributions from higher excited states.

The remaining possibility is that the two lower exciton states arise from a splitting in the 1*s* orbital state because of valley-orbit interaction. On this model these two exciton states are derived from different linear combinations of conduction-band states. The 1*s* orbital states of shallow donors in silicon are split by the impurity potential into a singlet $1s(A_1)$ and a closely spaced doublet $1s(E)$ and triplet $1s(T_1)$.[18] A similar valley-orbit splitting will occur in the free exciton. The magnitude of this splitting is enhanced by "dielectric breakdown" effects in the electron-hole interaction potential at short range.

A recent piezo-optical study of weakly bound indirect excitons in silver bromide[24] has revealed a valley-orbit splitting ΔE with a value of $\Delta E/E_x(0.22)$ comparable with the value reported for silicon in the present paper (~0.19). The type of splitting discussed by McLean and Loudon cannot occur in silver bromide because of the particular form of its band structure at the indirect gap. The splitting of the free exciton in silver bromide caused by electron-hole spin-spin interaction is apparently too small to be observed, as is so for silicon. We presume that the splitting between free excitons derived from the doublet and triplet electron states in silicon is also too small to be resolved experimentally, as would be anticipated from the relative magnitudes of the singlet-triplet and triplet-doublet splittings observed for shallow donor states in silicon.[25] These small unresolved splittings may vitiate the estimates of the low-temperature exciton-lattice relaxation times made in Sec. III.

According to the above interpretation, assuming that the singlet state lies lowest, the calculated intensity ratio of the absorption components with thresholds at E_2^{TO} and E_1^{TO} (Fig. 2) is 5, i.e., the absorption into the singlet state is just $\frac{1}{6}$ of the total absorption into the six conduction-band valleys. This result is derived in an appendix under some simplifying assumptions. This theoretical absorption ratio is of the order of the experimental ratios for the TO- and TA-phonon-assisted transitions contained in Eqs. (3) and (4), although the experimental ratios are slightly larger (~7). The experimental ratio is very sensitive to the strengths of the weaker components E_1^{TO} and E_1^{TA}. These components are difficult to measure precisely, since they only extend below the stronger components E_2^{TO} and E_2^{TA} for a very small energy interval (Fig. 1).

Transitions between these valley-orbit states of the free exciton are wave-function forbidden (*s*- to-*s* transition). Deviations from the thermal equilibrium value of the population ratio of these states may occur at low temperatures if phonons of symmetry type required to mix *s* and *p* states become frozen out. This effect is presumably responsible for the lack of thermalization in the low-temperature luminescence spectrum reported in Sec. III B.

V. SUMMARY

Fine structure has been resolved in the bands due to the creation and annihilation of free excitons present in the absorption and luminescence spectra of floating-zone-refined single crystals of silicon. This structure is identified with a splitting in the 1*s*-like envelope state of the free excition arising from the valley-orbit interaction. The magnitude of this splitting, ~1.9 meV, is qualitatively consistent with expectation for the weakly bound exciton according to similar effects recently reported in indirect exciton states in silver bromide and the magnitude of central cell effects in shallow donor states in silicon. The ratio of the absorption strengths for these states, calculated assuming that the lowest-exciton state is derived from electrons whose wave functions are made up from a symmetrical linear combination of states from the six equivalent lowest-conduction-band minima in silicon, is in fair agreement with experiment. Other potential sources of splitting, including *j*-*j* interaction and the effect of the anisotropy of the electron effective mass, do not produce experimentally detectable consequences. Further structure observed in the absorption spectra, for each phonon which

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[23] Y. Yafet, J. Phys. Chem. Solids **26**, 647 (1965).

[24] G. Ascarelli, Phys. Rev. Letters **20**, 44 (1968).

[25] R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, A1246 (1965). The ratio of the valley-orbit splitting energy D to the $1s(A_1)$ ground-state energy reported by Aggarwal and Ramdas for phosphorus donors (~0.26) is very similar to the ratio $\Delta E/E_x$ proposed for the free exciton in silicon from the present work. This comparison should be significant, since phosphorus and silicon are relatively similar in size and electronegativity and should, therefore, exhibit similar central cell corrections.

assists the indirect transitions, is identified with an excited orbital state of the free exciton and with the onset of free-carrier absorption, in agreement with MMQR. The binding energies of the various exciton states and the low-temperature indirect energy gaps are tabulated.

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APPENDIX

We show here that for a semiconductor having a valence-band maximum at $k=0$ and N equivalent conduction-band minima, the intensity of the indirect transition to the "singlet" exciton states[26] is just $1/N$ of the total intensity of transitions to the manifold of all the lowest exciton states in the N valleys. To make clear what is meant by "the lowest exciton states in the N valleys," we consider as an example silicon and neglect the spin-orbit splitting as well as the spin-spin splittings. It is then permissible to ignore the spin degree of freedom altogether, and, in the effective-mass approximation, the three valence-band states (x, y, z of $\Gamma_{25}{}^{+}$) interacting with the electron state Δ_1 of one valley will give rise to three exciton levels. These will be split[20] (the physical origin of the splitting is the anisotropy of the conduction-band effective mass) into a singlet $\Delta_2{}'$ and a doublet Δ_5. The magnitude of this splitting, as mentioned in Sec. IV, is estimated[20] to be very small (~4%) compared to the exciton binding energy, and we neglect it altogether. There will then be three lowest exciton states per valley, and the "manifold of all the lowest states in the N valleys" will contain 18 states. The "singlet" states from the six valleys are by definition the symmetric linear combinations of excitons from each valley, each exciton in the sum having the *same* valence-band hole. There will, thus, be three singlet exciton states (corresponding to x, y, z), and under the cubic group they will transform as $\Gamma_{25}{}^{+}$.

We now assume that these three states are split off from the remaining fifteen because the symmetric envelope function allows the electron and hole to spend more time near each other and to increase their binding energy. This is the essential splitting which is assumed responsible for the separation of the absorption thresholds $E_1{}^{\mathrm{TO}}$ and $E_2{}^{\mathrm{TO}}$ in Fig. 1, and we see that it separates the exciton levels into two groups with weights 1 and N, respectively.

In silicon, the spin-orbit splitting of the valence band is about four times the exciton binding energy, and it is more appropriate to consider the infinite spin-orbit splitting case. The four states of $\Gamma_8{}^{+}$ combine with the 6×2 conduction states to give 48 exciton states, eight of which are "singlets" (they give rise to the representations $\Gamma_8{}^{+}\times\Gamma_6{}^{+}=\Gamma_{12}{}^{+}+\Gamma_{15}{}^{+}+\Gamma_{25}{}^{+}$, but the degeneracy between them is not removed in our approximation).

To prove our assertion, it is not necessary to write down explicit exciton wave functions. The final states of the system are products of a "lowest" exciton state formed from the N valleys, and a phonon state (for definiteness only phonon emission is considered). The intensity is obtained by summing the modulus square of the matrix element over all final exciton states and all phonon states. According to the principle of spectroscopic stability (the sum over a set of degenerate states is independent of the specification chosen for the states), for each electronic state, the sum over the phonons is independent of the particular labeling chosen for the phonons, so we can use the usual characterization of the phonons by a wave number and a polarization. The same argument is valid for the electronic states, and in computing the intensity of the transition to the totality of lowest lying excitons, we can use exciton states that are confined to a single valley. We write then, schematically, the wave function for one of the final states of the system as

$$|\Psi_f(j,\lambda,\alpha)\rangle = a_{-\mathbf{K}_j,\lambda}{}^{\dagger}\Phi_j{}^{\dagger}(\alpha)|\Psi_0\rangle\,, \tag{A1}$$

where $|\Psi_0\rangle$ is the ground state of the crystal, $\Phi_j(\alpha)$ creates an exciton on valley j with internal state α, and $a_{-\mathbf{K}_j,\lambda}{}^{\dagger}$ creates a phonon $-\mathbf{K}_j$ with polarization λ. The total intensity is then

$$I=\sum_{j,\lambda}\sum_{\alpha}\sum_{m}\left|\frac{\langle\Psi_0|\Phi_j(\alpha)a_{-\mathbf{K}_j,\lambda}\mathcal{H}_{\mathrm{ph}}|\Psi_m\rangle\langle\Psi_m|\mathcal{H}_{\mathrm{rad}}|\Psi_0\rangle}{E_0-E_m+\hbar\omega}\right.$$
$$\left.+\sum_{m}\frac{\langle\Psi_0|\Phi_j(\alpha)a_{-\mathbf{K}_j,\lambda}\mathcal{H}_{\mathrm{rad}}|\Psi_m\rangle\langle\Psi_m|\mathcal{H}_{\mathrm{ph}}|\Psi_0\rangle}{E_0-E_m-\hbar\omega_{j\lambda}}\right|^2, \tag{A2}$$

where $\mathcal{H}_{\mathrm{ph}}$, $\mathcal{H}_{\mathrm{rad}}$ are the electron-phonon and electron-photon interactions, $\hbar\omega_{j\lambda}$ and $\hbar\omega$ are the phonon and photon energies, respectively, and the summation is over all intermediate states.

The singlet states with one phonon can be taken as

$$\Psi_s(j,\lambda,\alpha)=a_{-\mathbf{K}_j,\lambda}{}^{\dagger}N^{-1/2}\sum_{(i)}\Phi_i{}^{\dagger}(\alpha)|\Psi_0\rangle\,. \tag{A3}$$

When these are substituted into Eq. (A2), for fixed j, only the term with $i=j$ gives a nonzero contribution because of momentum conservation. The total transitions to the singlet states are, therefore, given by an expression identical with (A2), except that each term in the matrix element is multiplied by $N^{-1/2}$, i.e., the transition rate to the singlet states is $1/N$ of the total rate.

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[26] "Singlet" is written with quotation marks because in our approximation, as will be apparent shortly, there are $n_v\times n_c$ singlet states degenerate with each other, n_v and n_c being the degeneracy of the valence and conduction band, respectively.