Detailed Ground- and Excited-State Spectroscopy of Indirect Free Excitons

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Low-noise, high-resolution, far-infrared absorption spectra of free excitons in silicon are presented as a function of temperature. A complex thermalizing structure is revealed, resolving for the first time the electron-hole exchange splitting of an indirect-free-exciton ground state. A remarkable simplification of the spectrum is achieved with uniaxial stress. The relative intensities of the transitions suggest that the existing model for the free-exciton excited-state structure may be flawed, and an alternative scheme is proposed.

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Many of the fundamental optical properties of semiconductors are governed by free excitons (FE), mobile complexes of an electron (*e*), and a hole (*h*) bound together by the Coulomb interaction.[1] As FE are the simplest possible excitonic species, they occupy the same central position in excitonic physics as the H atom in atomic physics. Theoretical descriptions of the FE ground and excited states must incorporate the added complexities of the semiconductor band structure, such as additional degeneracies and nonspherical effective masses for both the *e* and *h*. Nevertheless, the most detailed existing theory[2] of the FE structure in Si (and Ge) is currently considered to be in excellent agreement with the available experimental results.[3]

We present here new measurements of the far-infrared (FIR) absorption spectra of FE in Si which provide greatly enhanced resolution and signal-to-noise ratio compared with the previous results.[4] These new measurements cast some doubt on the adequacy of the existing[2] theoretical description of the FE in Si. We propose an alternative framework which may be better able to describe the FE excited states. We also observe the first resolved splitting of an indirect FE ground state due to the *e*-*h* exchange interaction, which is found to be surprisingly large, comparable in magnitude to the much-studied mass-anisotropy[2,5,6] splitting. Finally, a dramatic simplification of the spectrum is achieved by the application of a large uniaxial stress, which removes much of the conduction- and valence-band degeneracy.

The results presented here were obtained with a Bruker IFS 113-V Michelson interferometer coupled to a Vari-Temp sample chamber and 1.4-K Ge bolometer. The ultrahigh-purity Si samples were mounted in a strain-free manner and immersed in liquid He. The temperatures quoted here are the bath temperatures as determined from the He vapor pressure. The FE were generated with 514-nm excitation from an Ar$^+$ laser, which was defocused over a large sample area to preclude the formation of electron-hole droplets. Samples of ultrahigh-purity Si obtained from two different manufacturers produced identical FE absorption spectra.

In Fig. 1 we show typical FIR absorption spectra due to transitions from the 1*S*-type FE ground-state multiplet to various *P*-type FE excited states. The excess noise in the 4.2-K spectrum results from bubbles in the liquid He. The increase of the linewidths with increasing *T* is due to the small dependence of the FE transition en-

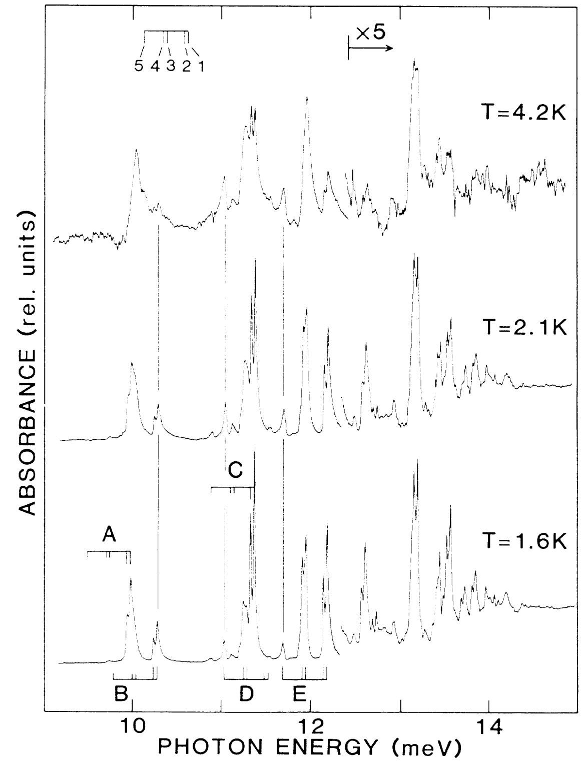

FIG. 1. FE absorption spectra in Si taken at 1.6, 2.1, and 4.2 K. The five identifiable 2*P*-type transitions are labeled A through E. The fivefold bracket at the top left (and also associated with A through E) indicate fine structure from the five (1 through 5) ground-state sublevels. Long tick marks on the brackets indicate transitions which couple strongly, while short tick marks indicate the location of transitions with weak or unobservable coupling.

ergies on the translational kinetic energy of the FE.[2] This effect explains the lower resolution of the previous[4] spectra, obtained at ≥ 8 K. By looking for repetitive, thermalizing fine structure in the spectra, one can identify multiplets arising from transitions from the split ground state to various discrete excited states. Five such identifications can be made with certainty, as indicated by the fivefold (A thru E) component (1 through 5) brackets on the 1.6-K spectrum of Fig. 1. Here 1-5 label the five observed ground-state components, and A-E label the lowest five P-type excited states. The energies of these states above the lowest ground-state component 1, are given on the left side of Table I.

We will begin by considering the observed fivefold ground-state splitting. It has long been known that the FE ground state in Si is split into two levels having symmetry Δ_7 (lowest in energy) and Δ_6 of the C_{4v} group appropriate for FE in Si as a result of the lifting of the valence-band degeneracy by the electron effective-mass anisotropy.[7] The measurement of this splitting for the Si FE has led to much controversy,[5] since all previous attempts used the poorly resolved near-infrared (NIR) transitions in which FE are created (absorption) or annihilated (luminescence). It is clear from Fig. 1 that much better results can be obtained from FIR absorption studies. The additional ground-state structure evident in our results must originate from e-h exchange splittings, which until now have not been observed for an indirect FE, although their possible influence on the NIR transitions has received some consideration.[6] In that study,[6] only a twofold splitting of Δ_7 and Δ_6 was considered, but group theory reveals that a threefold splitting of each sublevel is allowed. In the C_{4v} point group the electrons transform as Δ_6 and the holes as Δ_7 and Δ_6, hence e-h exchange can split the Δ_7 and Δ_6 FE ground states into the triplets $\Delta_6 \times \Delta_7 = \Delta_3 + \Delta_4 + \Delta_5$ and $\Delta_6 \times \Delta_6 = \Delta_1 + \Delta_2 + \Delta_5$, respectively, where Δ_5 is doubly degenerate and Δ_1 through Δ_4 are nondegenerate.

If we make the very reasonable assumption that the exchange splittings of the P-type excited states are negligible, then the FIR results can be used to separate those ground-state components originating from either Δ_7 or Δ_6, since while these may couple differently to different P states, the exchange split substates arising from Δ_7 will couple identically to a given P state (taking into account degeneracy and thermal population factors). This is because each P state will contain all the degenerate states possible from e-h coupling. While the distinct ground-state components arising from e-h coupling will couple differently to the various (degenerate) e-h coupling states associated with a given P state, the *total* coupling to the P state will be the same for all e-h split ground-state components arising from a given overall ground state (Δ_6 or Δ_7).

TABLE I. Energies in meV of various Si FE states above the ground state.

Experiment Level	 Energy	Unstressed Theory[b] Level $L(F,F_z)$	 Energy	580 MPa ⟨001⟩ stress Level	 Energy[a]
2	0.042			2	0.19
3	0.233			$2P_0$	10.31
4	0.273	$1S(\frac{3}{2},\pm\frac{1}{2})$	0.46	$2P\pm$	10.77
5	0.486			$3P_0$	12.28
A	9.991	$2P(\frac{3}{2},\pm\frac{3}{2})$	10.01	$3P\pm$	12.49
B	10.287	$2P(\frac{3}{2},\pm\frac{1}{2})$	10.37	$4P_0$	12.98
C	11.374	$2P(\frac{5}{2},\pm\frac{1}{2})$	11.38	$4P\pm$	13.10
D	11.522	$2P(\frac{5}{2},\pm\frac{5}{2})$	11.47	$5P_0$	13.30
E	12.183	$2P(\frac{5}{2},\pm\frac{3}{2})$	12.04	$5P\pm$	13.37
		$2P(\frac{1}{2},\pm\frac{1}{2})$	12.31		

[a] ±0.01 meV.

[b] References 2 and 4.

From Fig. 1 we can identify cases where ground-state levels 1-5 all couple to a given excited state (transition E and to a lesser extent B), where only 1 and 2 couple strongly (transitions A and C), and where only levels 3-5 couple strongly (transition D). Thus we can argue that 1 and 2 are the e-h exchange split Δ_7 FE ground-state levels (one of the allowed splittings must be too small to be observed), while 3-5 are the states resulting from the exchange splitting of Δ_6. The thermalization of the spectra clearly support this ordering. It is interesting to note that the e-h exchange splittings are therefore comparable in magnitude to the mass-anisotropy splitting, and that the FE ground state is considerably more complicated than was assumed[5,6] in the NIR measurements.

We now consider the P-type FE excited states revealed in Fig. 1. Only transitions A-E have been labeled, since only these are clearly $2P$ type and have readily identifiable couplings to the five ground-state levels. The energies of these transitions are in quite good agreement with theory[2] and earlier measurements[4] in which only three components could be resolved. However, we will show that the intensities of some of the transitions are not in agreement with the predictions of this theory.

Lipari and Altarelli[2] calculated the FE ground- and excited-state energies using a model very similar to one previously applied to acceptor states. In this model the states are labeled by the total (hole+orbital) angular momentum F and its projection along the axis of the conduction-band ellipsoid, F_z. In this notation the Δ_7 and Δ_6 FE ground states are $1S^{3/2}_{\pm 3/2}$ and $1S^{3/2}_{\pm 1/2}$, respectively, and the $2P$ states are $2P^{F}_{\pm F_z}$, where $F = \frac{1}{2}$, $\frac{3}{2}$, or $\frac{5}{2}$. The calculated energies of these states are given in Table I.

We have calculated the $1S \rightarrow 2P$ relative oscillator strengths for these states by approximating each state by the leading term for which it is named, taking the FE to be at rest, and averaging over all photon polarization and propagation directions. While there are several discrepancies between this calculation and the observed results, the most serious is for the lowest-lying P state (A transition), which is seen to couple *only* to the Δ_7 ground state. Our calculations predict that $2P^{3/2}_{\pm 3/2}$ (and $2P^{3/2}_{\pm 1/2}$) should couple to *both* Δ_7 and Δ_6 ground states in disagreement with experiment.

This may reflect an inadequacy in the acceptorlike model used by Lipari and Altarelli.[2] Instead, one could model the $2P$-type envelope of the e-h relative motion in terms of the $2P$ donor states. For the neutral donor, $2P$ splits into $2P_0$ and $2P_{\pm}$, with $2P_0$ lowest in energy. If the lowest FE excited states are $2P_0$ type, the inclusion of the hole angular momentum produces two states, $2P_0{}^{3/2}_{\pm 3/2}$ and $2P_0{}^{3/2}_{\pm 1/2}$. If the ordering of these is the same as it is for the ground state ($\pm\frac{3}{2}$ lowest), then the experimental results can be explained, since $2P_0{}^{3/2}_{\pm 3/2}$ couples only to $1S^{3/2}_{\pm 3/2}$ (Δ_7), while $2P_0{}^{3/2}_{\pm 1/2}$ couples only to $1S^{3/2}_{\pm 1/2}$ (Δ_6). The $2P_{\pm}$ envelope transforms as Δ_5 of C_{4v}, and coupling this with the Δ_7 and Δ_6 holes produces four levels: $\Delta_5 \times \Delta_7 = \Delta_6 + \Delta_7$ and $\Delta_5 \times \Delta_6 = \Delta_6 + \Delta_7$. In the absence of mixing, $\Delta_5 \times \Delta_7$ $2P_{\pm}$ states should couple only to the Δ_7 ground state, and $\Delta_5 \times \Delta_6$ $2P_{\pm}$ states to the Δ_6 ground state (transitions C and D), but mixing can relax these constraints (transition E).

A remarkable simplification of the FE spectrum can be achieved with large ⟨001⟩ uniaxial stress as shown in Fig. 2. The stress lowers the energy of the two conduction-band valleys oriented along the stress axis, and removes the valence-band degeneracy, leaving only Δ_6 holes, whose constant-energy surface in k space is also an ellipsoid of revolution oriented along the stress axis. Thus the FE becomes essentially hydrogenic, except for the P_0-$P_{\pm}$ splitting, which can be nicely separated by polarization selection, as shown in Fig. 2.

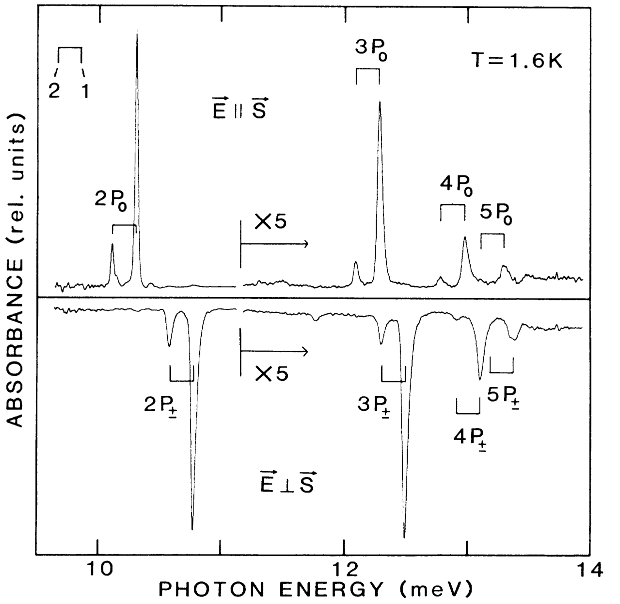

FIG. 2. FE polarized absorption spectra in Si at 1.6 K under an ⟨001⟩ uniaxial stress of 580 MPa. The double bracket on all the transitions indicates the fine structure resulting from the doublet ground state.

Figure 2 also reveals an identical doublet splitting of all the transitions, which has been found to thermalize. This ground-state splitting can only arise from e-h exchange, since all other degeneracies have been removed by the stress. The energies of all of these transitions above the lowest ground-state level (1) are given on the right-hand side of Table I. The energy spacings agree closely with those calculated by Faulkner[8] with use of the appropriate e (Ref. 9) and h (Ref. 10) effective masses. A preliminary study of the FE absorption spectrum as a function of ⟨001⟩ stress is in agreement with our proposed new model for the FE P states. As the stress is increased, the (A,B) transitions of Fig. 1 were seen to evolve into the $2P_0$ transition of Fig. 2, while the (C,D) lines of Fig. 1 evolved into the $2P_{\pm}$ line of Fig. 2

In conclusion, we have presented greatly improved FIR absorption spectra of the FE in Si, which reveal for the first time the complete ground-state structure of an indirect FE. A remarkable simplification of the spectrum was achieved with uniaxial stress. We have proposed a new model for the FE P-type states which may be better able to describe the observed relative transition strengths. It would be interesting to investigate whether a variational calculation based upon the type of trial function proposed here could give accurate values of the P-state binding energies.

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