Far-Infrared Absorption Spectrum of Be-Related Bound Excitons in Silicon

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The first measurement of the far-infrared absorption spectrum of a bound exciton is reported. This spectrum reveals the odd-parity excited states of the exciton, which cannot be observed by other means. The excited-state spectrum is found to be in excellent agreement with those of acceptors in Si, verifying earlier predictions of the level structure for isoelectronic bound excitons.

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Since their discovery in Si in 1960,[1] bound excitons (BE) have been the subject of wide-ranging research.[2] Virtually all previous investigations involved the study of near–band-gap photons which are either absorbed to create BE in ground or excited states (absorption and excitation spectroscopy), or emitted when BE in the ground or excited states are annihilated (luminescence spectroscopy). As a result of selection rules, such studies are usually restricted to states of only one parity. For example, much is known about the even-parity states of the many donor, acceptor, and isoelectronic bound excitons in Si, but nothing had previously been discovered regarding their odd-parity excited states. We report the first far-infrared (FIR) spectrum of the transitions from the even-parity ground state of a BE to its odd-parity excited states. Such studies should also be feasible for other BE, with the potential of observing an entire class of excited states heretofore inaccessible.

Unlike the more common donor or acceptor FIR absorption studies, the observation of BE FIR absorption requires the use of an excitation beam to maintain a population of BE. The experimental arrangement is thus similar to that used to observe FIR absorption of free excitons in Si.[3] For our initial study, an isoelectronic bound exciton (IBE) was selected, since the long lifetime of IBE as compared to donor or acceptor BE simplifies the task of maintaining an observable concentration. Of the many IBE now known to exist in Si, the Be-related[4-6] IBE was chosen, since unlike some of the other candidates, the binding center responsible for this IBE is known to exist in high concentrations ($\sim 10^{16}$ cm^{-3}).[6]

The Be-doped samples used in this study were the same ones used in previous near-infrared (NIR) photoluminescence, absorption, and excitation spectroscopy experiments.[6] Figure 1 shows the transmission of the sample (top curve) without correction for instrumental response. The lines α, β, γ, and δ are present in the crystal without irradiation with band-gap light and they persist up to a temperature of 30 K. Since the material is p type the absorption is presumably due to holes bound to some charged trapping site. The lines do not correspond to any known acceptor absorption and are probably associated with beryllium, the major active impurity. The separation between the component lines is typical of the higher states of a shallow acceptor in silicon starting with a line at 17.2 meV that is par-

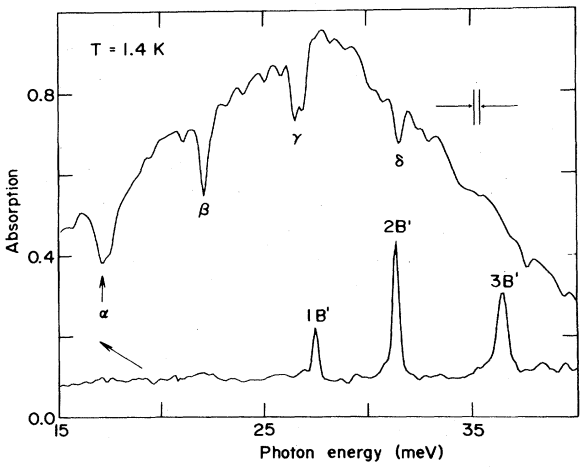

FIG. 1. Uncorrected FIR absorption spectrum of Be-doped Si sample without above–band-gap excitation (top), and the change in the FIR absorption induced in the same sample by chopped above–band-gap excitation (bottom).

tially hidden by a line at 17.5 meV due to a Mylar vacuum window in our cryostat. The ionization potential can be estimated to be around 31 meV. From the strength of the absorption we calculate the concentration of the center to be 5×10^{13} cm^{-3} with the assumption of an effective mass $m^*=0.4$.

The lower curve of Fig. 1 shows the induced FIR absorption at an absorbed power of 40 mW of above-band-gap light (the red line of the krypton laser). Three lines dominate the spectrum. We call these lines, $1B'$, $2B'$, and $3B'$. The line marked $2B'$ is close to the absorption line γ but the difference in position is outside the range of our experimental error. The areal concentration of the center giving rise to these induced lines can be estimated from their strength to be 4.0×10^{12} cm^{-2} with the assumption of an effective mass $m^*=0.4$. The excitation depth has not been determined but is certainly much less than the ~1-mm sample thickness.

Figure 2 shows the induced absorption spectrum of the same sample at three different temperatures, 1.4, 8, and 15 K. At 8 K new lines labeled $1B$, $2B$, and $3B$ appear on the low-energy sides of the $1B'$, $2B'$, and $3B'$ lines, each separated by 0.62 ± 0.08 from the low-temperature line. A new isolated induced line can also be seen at 22.13 meV. Three additional lines can be resolved above the noise level at 15 K. They are denoted $1A$, $2A$, and $3A$, and each is separated from its related B' line by 2.5 ± 0.1 meV.

These results can be readily understood by comparing the IBE level structure as determined from NIR measurements[6] with the energies of the induced FIR absorption lines as is shown in Fig. 3. The IBE ground state is split by j-j coupling and by the axial strain field of the defect into four closely spaced levels, as is typical for IBE bound to axial defects in other semiconductors.[2] Three of these levels (A, B, and B') can be observed in ordinary NIR photoluminescence spectra, depending upon the thermal populations of the initial states, while the fourth (B'') line can only be observed in the presence of a magnetic field.[5] This quartet of IBE ground states serves as the initial states of the FIR absorption transitions. At 1.4 K only the lowest (B') state is populated, which results in a simple FIR spectrum showing three excited states

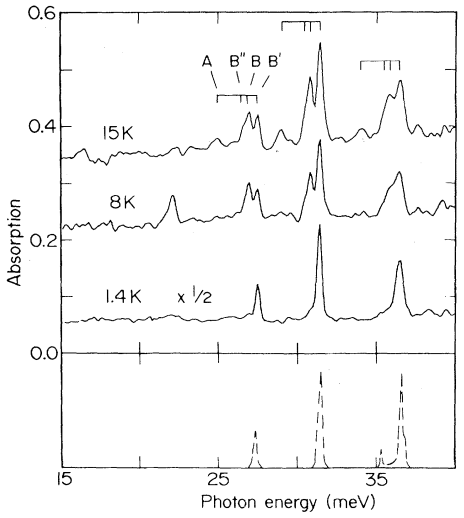

FIG. 2. Induced absorption in the same sample at 1.4, 8, and 15 K. The three brackets above the absorption lines show the predicted locations of transitions from the B, B'', and A levels of the ground state based upon the observed locations of transitions from the B' initial state observed at the bottom (taken from Ref. 9) shows the FIR absorption spectrum of the boron acceptor shifted down by 3.0 meV.

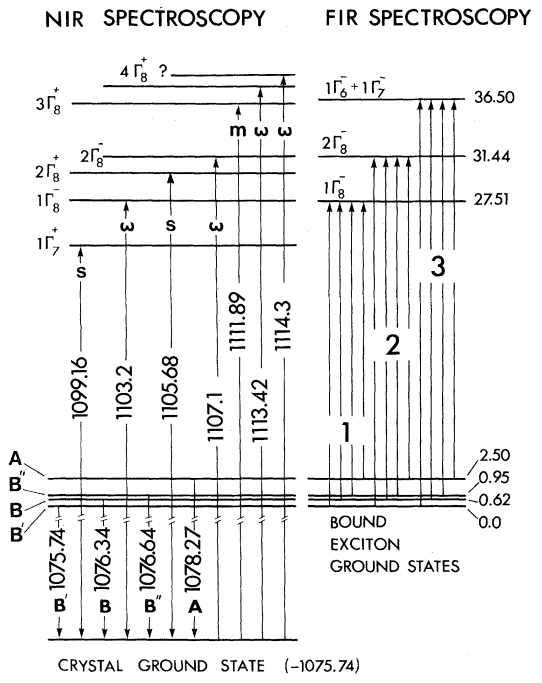

FIG. 3. A comparison of the levels and energies determined by NIR and FIR spectroscopy. The lowest IBE ground state, B', is taken as the zero of energy. Except for the crystal ground state, all energies are to scale. The s, m, and w on the NIR excited-state transitions stand for strong, medium, and weak. The symmetry labels on the excited states are those derived in the text from a comparison with acceptor spectra. All energies are in megaelectronvolts.

(1, 2, and 3). At 8 K the B state, 0.6 meV above the B' state, becomes populated and FIR transitions between the B state and the 1, 2, and 3 excited states become possible. At 15 K the A state which lies 2.5 ± 0.1 meV above the B' state is significantly populated and FIR transitions from A to the 1, 2, and 3 excited states are also observed.

As summarized in Table I, the FIR splittings in all cases agree with those determined from NIR photoluminescence. Also, the 8- and 15-K spectra reveal a shoulder displaced 0.3–0.4 meV below each B line, in excellent agreement with the predicted[5] zero-field location of the B'' state. Further evidence that the NIR and FIR spectra arise from the same defect is provided by the exact coincidence between the energies of the 1 and 2 excited states seen in the FIR spectra with two very weak lines seen in the NIR excitation spectra, as summarized in Fig. 3 and Table I. The appearance of these odd-parity excited states in the NIR spectra, albeit very weakly, reveals that the selection rules are not perfectly obeyed, but we note that none of the even-parity excited states are visible in the FIR spectra.

One puzzle is the absorption line seen at 22.13 $\pm$ 0.04 meV in the 8-K spectrum. This could be a transition from the B state to a fourth odd-parity excited state, but the disappearance of the line at 15 K is unexpected. As a result we have not included it in our level scheme.

All of the observed excited states can be quantitatively accounted for by a model for IBE states proposed by Hopfield, Thomas, and Lynch[7] which was later found to be valid for the even-parity states of IBE bound to N pairs in GaP.[8] In this model a deep isoelectronic binding center first binds an electron (hole) into a very localized state, after which a hole (electron) is bound in the Coulomb field of the first particle. Such an IBE is known as an isoelectronic acceptor (donor), and the excited-state spectrum of the loosely bound hole (electron) should be quite similar to that of an effective mass acceptor (donor).

As can be seen at the bottom of Fig. 2, the odd-parity excited-state spectrum of the boron acceptor,[9] when shifted down by 3 meV, mirrors the odd-parity excited-state spectrum of the Be-related IBE in every detail. Thus this IBE appears to be an isoelectronic acceptor with a hole binding energy of 3 meV less than that of boron,[10] or 43 meV. The excited states labeled 1, 2, and 3 correspond to the acceptor states $1\Gamma_8^-$, $2\Gamma_8^-$, and $(1\Gamma_7^- + 1\Gamma_6^-)$.[11]

The isoelectronic-acceptor assignment is further supported by a consideration of the even-parity excited states, which unlike the odd-parity states may be affected by the "central cell potential," particularly for low quantum numbers. The boron $3\Gamma_8^+$ state (as determined by acceptor BE two-hole spectroscopy)[12] lies 39.45 ± 0.1 meV above the ground state, while the corresponding Be IBE level (that responsible for the 1111.89-meV NIR transition) lies 36.15 ± 0.13 meV above the B' state. The difference between the two values is 3.3 ± 0.23 meV, in good agreement with the 3-meV difference in ground-state binding energies as determined from the FIR spectra. Similarly, the stronger NIR line at 1105.68 meV (29.94 ± 0.13 meV above the B' state) corresponds to the boron $2\Gamma_8^+$ excited state, which lies 32.39 ± 0.1 meV above the ground state. Again the difference in splittings of 2.45 ± 0.23 meV is in good agreement with the FIR value of 3 meV, given that $2\Gamma_8^+$ is more likely to be shifted by central-cell effects. Finally, the weakest NIR excited state (1114.3-meV transition) matches the expected location of the $4\Gamma_8^+$ level.

At first glance, the strongest NIR excited state at 1099.16 meV (23.42 ± 0.13 meV above the B' state) does not fit into the known acceptor even-parity excited-state spectrum, but one must remember that acceptor BE two-hole spectra only reveal those even-parity states which have an overlap with the acceptor BE hole wave functions. A different type of acceptor even-parity excited state has been observed in Raman scattering,[13] and was later shown to be a split-off $1\Gamma_7^+$ state.[11] For boron this state lies 23.4 meV above the $1\Gamma_8^+$ ground state,[13] exactly the same splitting seen in the Be-related IBE. This close agreement is explained by calculations[11] showing the $1\Gamma_8^+$ to $1\Gamma_7^+$ splitting to be independent of changes in

TABLE I. Comparison of energy-level differences as determined by NIR and FIR spectra.

Assignment	NIR splitting (meV)	FIR splitting (meV)
B'-B	0.60 ± 0.10 [a]	0.62 ± 0.08
B'-B''	0.9 [b]	0.95 ± 0.10
B'-A	2.53 ± 0.13 [a]	2.50 ± 0.01
B'-1	27.46 ± 0.20 [a]	27.51 ± 0.03
B'-2	31.36 ± 0.20 [a]	31.44 ± 0.03
B'-3	...	36.50 ± 0.04

[a]Ref. 6. [b]Ref. 5.

parameters which produce large variations in the ground-state binding energy. In this connection we also suggest that a strong NIR transition observed[14] in the excited-state spectrum of another IBE in Si (there labeled E, 24.34 meV above the lowest ground state) is not in fact a parity-forbidden $1\Gamma_8^-$ transition as suggested, but rather the allowed transition to the same $1\Gamma_7^+$ state.

These studies provide strong evidence of the isoelectronic-acceptor nature of the Be-related IBE, but previous work has been based upon an isoelectronic-donor model.[4-6] One of the arguments used to support the previous assignment dealt with the Γ_5 phonon sidebands, which interact particularly strongly with holes.[5] Since the electron-phonon interaction is largest for the more strongly localized particle, it was suggested that this was the hole.[5] The phonon sidebands do not, however, reflect the overall Γ_5 spectrum but are restricted to very-low–wave-vector acoustic and LO branch phonons, which is more consistent with a *weakly* bound hole. This behavior closely parallels the case of O in ZnTe.[7]

In conclusion, we have observed the first FIR spectrum of the odd-parity excited states of a BE, and have identified all of the stronger even- and odd-parity states with known acceptor excited states. This technique should be applicable to many other BE systems, particularly if it were extended by use of resonant excitation of the BE population, for example with a color-center laser.[14] This would allow the selective volume excitation of thick samples containing low densities of binding centers.

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