PHYSICAL REVIEW B VOLUME 40, NUMBER 14 15 NOVEMBER 1989-I

Optical properties of the sulfur-related isoelectronic bound excitons in Si

D. J. S. Beckett, M. K. Nissen, and M. L. W. Thewalt
Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(Received 9 February 1989)

We present a detailed spectroscopic investigation of excitons bound to two recently discovered sulfur-related isoelectronic centers in Si with photoluminescence (PL) emissions near 1.3 and 1.5 μm. High-resolution photoluminescence and photoluminescence-excitation (PLE) spectroscopy were combined with the new far-infrared exciton-absorption spectroscopy (FIEAS) technique to reveal the electronic structure of these bound excitons. Striking similarities between the two centers were observed with all three techniques. Low-temperature PL reveals a low-energy dipole-forbidden ground-state transition. The FIEAS results show that the isoelectronic bound excitons have donorlike electronic excited states with electron binding energies of 65.28 and 66.21 meV for the shallow and deep centers, respectively. These energies are twice that of the donor effective-mass model. The determination of the electron binding energies by FIEAS allows the identification of many of the transitions observed in PL and PLE.

I. INTRODUCTION

One subject of focus in the study of the many properties of bound excitons (BE's) in semiconductors[1-4] is that of their excited-state structure. This field has drawn particular attention because of the comparisons and contrasts that can often be made between excitons and atomic hydrogen,[1,3,4] as with donor and acceptor impurities. The study of the electronic structure of BE's also aids in the understanding of the physical characteristics of the binding center itself by providing information on such properties as the site symmetry, the affinity of the center for holes and electrons, and the nature of the central-cell potential. In addition to characterizing the optical properties of the BE's, it is hoped that the study of the BE excited states will yield information that will ultimately help determine the actual atomic arrangement of the binding center.

One particular type of BE is the isoelectronic bound exciton (IBE),[3-7] in which an exciton becomes bound to an impurity or defect center which behaves neither as a donor nor an acceptor. The electronic structure of the IBE can often be described in terms of the model of Hopfield, Thomas, and Lynch (HTL).[5] This model describes cases where the binding center tightly localizes a hole (or electron) which in turn binds an electron (hole) via the Coulomb interaction, and the resulting IBE has donorlike (acceptorlike) excited states. Differences from true donor or acceptor excited states may occur due to a variety of effects. Examples include the reduced symmetry or extended nature of the binding center, or the nonlocalized nature of the central charge relative to a true donor or acceptor.

In another model,[6] *both* the electron and hole can become localized due to the strain field of the isoelectronic center. Analogies with the hydrogen atom are no longer appropriate and no detailed theory exists to describe the excited states of such a system. However, the electron and hole states would be similar to those of the conduction-band and valence-band edges, and the excited states should resemble those of a free exciton in a strain field of the same symmetry.

In the case of IBE's, the normal optical methods of obtaining information on the bare binding center do not apply, since as isoelectronic centers there are no binding-center (i.e., donor or acceptor) excited states to observe by far-infrared (FIR) absorption, nor are there two-electron or two-hole replicas to observe in the photoluminescence (PL) spectra. PL is useful, however, in the identification of IBE's through the observation of their long decay lifetimes and high radiative efficiencies. PL can also determine the total binding energy of the exciton, the energies of local phonon modes, and other properties related to the IBE ground state. PL alone, however, reveals little about the IBE excited-state structure. In order to obtain information on the IBE excited states, and thus the binding centers as well, techniques other than PL must be employed.

The standard method of probing the excited-state spectrum of a BE system is photoluminescence-excitation (PLE) spectroscopy.[8] In this technique luminescence is observed at the energy of one of the main PL lines or their phonon replicas, while a tunable excitation source resonantly creates the BE via their excited states. This method works best when the phonon-assisted absorption or absorption due to other competing processes is small compared with that of the no-phonon (NP) excited-state transitions. When phonon coupling is strong, however, the low-intensity NP transitions are easily obscured by the Stokes phonon sideband, and the electronic excited states are difficult to observe.

In such cases, a recently developed method of BE excited-state spectroscopy[9,10] can be most useful. This technique is far-infrared exciton-absorption spectroscopy (FIEAS), in which BE's are created via above-band-gap or resonant pumping, and then the ground-state to excited-state transitions of the BE are observed as a FIR-absorption spectrum, in close analogy with ordinary impurity FIR-absorption spectroscopy.

The FIEAS technique is not affected by the strong phonon coupling associated with the creation or annihilation of the IBE, as in PL and PLE, since the highly localized particle does not undergo a change of state. The transition of the weakly (Coulomb) bound particle from the IBE ground state to an excited state results in no significant phonon interaction. Thus, the FIEAS spectrum can be very sharp even for centers showing no electronic PLE transitions. FIEAS is, however, also useful even in the cases where results can be obtained using PLE. This is because of the complementarity of the selection rules, which predominantly allow even-parity excited states to be observed with PLE and odd-parity states with FIEAS. FIEAS was first applied to Be-related IBE's in Si,[9-11] and later to the Be and Zn double-acceptor BE's in Ge.[12]

In this paper we present a comprehensive study of the optical spectroscopy of two recently discovered luminescent centers in silicon doped with sulfur.[13,14] Based on the high radiative efficiency and long decay lifetimes, this emission was attributed to the decay of excitons bound to isoelectronic centers. The luminescence occurs at ~ 1.3 and ~ 1.5 μm, which we label the S_A and S_B systems, respectively. The fact that the luminescence can be detected at temperatures as high as 170 K raises interesting possibilities about Si-based light-emitting device applications for these or similar centers. Given the advanced state of Si microelectronics technology relative to that of GaAs and other materials, the capability of making an entirely Si-based optical component could be very useful in the future development of integrated optics.[15]

We have applied PL, PLE, and FIEAS to study the optical transitions related to these systems. Some of these results have been presented as examples of new methods of excited-state spectroscopy.[16]

II. EXPERIMENTAL METHOD

Reagent-grade sulfur was introduced by diffusion in the presence of O_2 gas into a number of samples of Czochralski-grown Si following Ref. 13. Diffusion of high-purity S (99.9999%) into ultrahigh-purity (UHP) float-zoned Si in the absence of O_2 was also done. To promote the formation of isoelectronic centers, the S-diffused samples were subjected to a rapid quench procedure.[13,17,18] The best results were obtained by heating the Si to an orange heat (about 900 °C) and using ethylene glycol as the quench, although ample photoluminescence was observed for all cases. After the heat treatment, the samples were given a quick etch in a 1:10 HF:HNO_3 solution to improve the surfaces for optical studies. The presence of most other common dopants (Ga, B, Al, As, and P) in the starting material had little effect on the Si:S IBE luminescence. The presence of In, however, resulted in the preferential formation of In-related isoelectronic centers,[19] and little evidence of the S centers was seen. From the UHP Si samples it was determined that while oxygen may aid in the incorporation of S into Si, it is not a constituent of the isoelectronic complex as earlier suggested.[14] This conclusion is supported by the fact that strong Si:S IBE luminescence and FIR-IBE absorption could be obtained from UHP Si samples diffused with high-purity S in the absence of O_2. Even if some O_2 were present in the ampoule, the diffusion coefficient of O into Si is almost 2 orders of magnitude lower than that of S.[20]

The majority of the PL measurements were performed on a Bruker IFS 113v Fourier-transform interferometer, using a Northcoast E0817S liquid-nitrogen-cooled intrinsic Ge detector. Preliminary measurements were made using an Ar^+-ion laser as the excitation source. The IBE can be more efficiently created, however, with the 1.06-μm line of a Nd:YAG (yttrium-aluminum-garnet) laser and this is the preferable excitation source. The 1.32-μm line of the Nd:YAG laser was also used for excitation in several measurements. As discussed in the next section, an interesting PL up-conversion process was observed. To study this effect, the 1.32-μm line of the Nd:YAG laser was used, together with a $\frac{3}{4}$-m double spectrometer because of its superior light-rejection capability. Photoluminescence-excitation spectroscopy was performed on both the S_A and S_B systems. Excitation was provided over the ranges 1.18–1.3 and 1.4–1.52 μm by a $LiNbO_3$ optical-parametric-oscillator (OPO) system, which is described in detail elsewhere.[21] The excitation had an average power of 30 mW with a linewidth between 0.5 and 1 meV. Luminescence was collected via the grating spectrometer and Ge detector. All PLE measurements were carried out with the samples immersed in superfluid He.

For PLE of the shallower S_A system, luminescence was collected from the phonon sideband at 900 meV (1.38 μm) rather than the NP transition at 968 meV. This step was taken to avoid interference with the PLE spectrum through Raman scattering of the incident excitation by the 64-meV O^Γ lattice phonon. Excitation luminescence from the deeper S_B system was collected at the lowest NP transition energy of 812 meV (1.53 μm). Raman scattering was not as strong in this spectrum and there was no need to move the spectrometer away from the NP transition to the phonon sideband.

The FIEAS was performed on the same interferometer as used for PL. FIR radiation from a globar source was shone lengthwise through a $2\times5\times10$-mm^3 heat-treated Si:S sample, and detected by a Ge bolometer held at 1.6 K. Bulk excitation was provided by the cw Nd:YAG laser operated at either 1.06 or 1.32 μm. The laser beam was elongated by a cylindrical lens and focused onto the 2×5-mm^2 narrow edge of the sample, at right angles with the FIR path. The scattered laser light was prevented from reaching the bolometer by black polyethylene filters.

III. RESULTS AND DISCUSSION

A. Photoluminescence spectroscopy

PL spectra of the two systems are shown in Fig. 1 at temperatures of 70, 35, and 8 K. The two spectra at higher temperatures, Figs. 1(a) and 1(b), agree with those previously reported[13,14] and are included for comparison with the 8-K spectrum of Fig. 1(c) which reveals new lower-energy NP transitions in both systems. At temper-

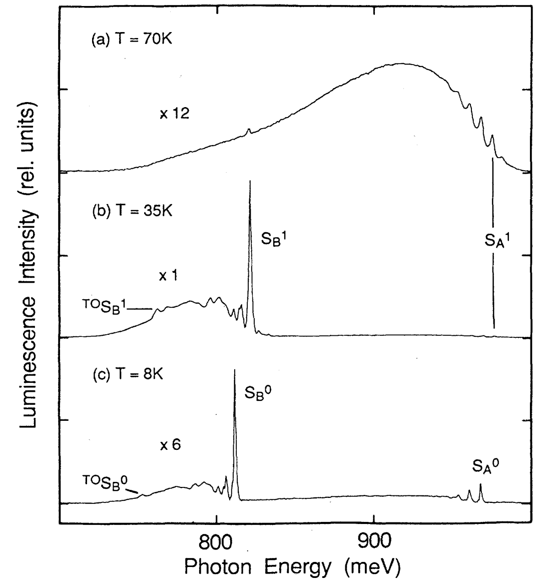

FIG. 1. Low-resolution, wide-spectral-range photoluminescence spectra showing large-scale features at 8, 35, and 70 K. Resolution is 1.4 meV.

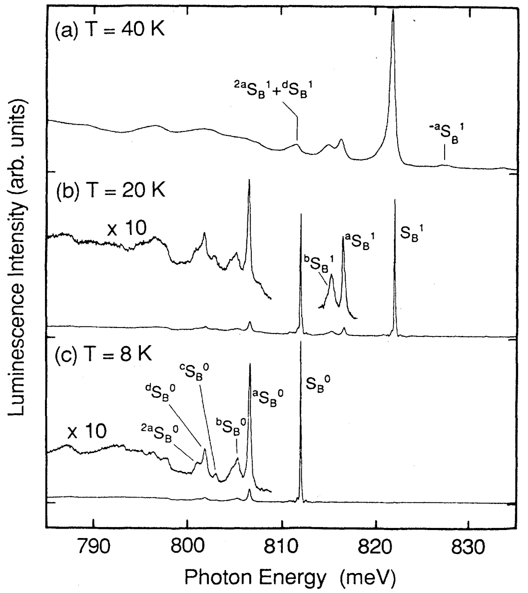

FIG. 2. High-resolution photoluminescence spectra of the S_B system at 8, 20, and 40 K showing temperature dependence of the no-phonon transitions and their local-mode phonon replicas. Selected regions of the 8- and 20-K spectra have been expanded by ten times for clarity. The labels are as explained in the text. Resolution is 0.09 meV.

atures between 1.6 and 10 K, they are the only NP transitions present, and only above these temperatures do the previously reported transitions at 821.9 and 977.1 meV appear. These new lines at 812.0 and 968.2 meV are thus identified as dipole-forbidden transitions to the crystal ground state from the lowest IBE ground states, giving exciton localization energies of 357.3 and 201.0 meV for S_B and S_A, respectively.

Also evident in the spectra of Fig. 1 is the strong degree of phonon coupling in both systems. This strong coupling, which is consistent with the observed large exciton binding energies, is predominantly to local-mode phonons, although the TO lattice phonon replica of the S_B electronic transitions are also visible.

High-resolution PL spectra are shown in Figs. 2 and 3. To label the transitions, the notation $^{m}S_A^n$ has been used, where n represents the initial IBE electronic state ($0 \equiv$ IBE ground state) and m labels the local-mode phonon (m represents cases where the phonon energy is subtracted from the electronic transition energy, and $-m$ cases where the phonon energy is added). Of the two systems, more structure is found in the S_B spectrum shown in Fig. 2 than in S_A (Fig. 3). In Fig. 2(a) there are at least four local-mode phonons, labeled a, b, c, and d. Also shown is a transition labeled $^{2a}S_B^0$ in which two type-a phonons are emitted.

The PL results are presented first so that the connection with previous work is more easily made. However, in order to begin consistent labeling of the various PL transitions, the knowledge gained through FIEAS that these IBE's are donorlike is used. The PL ground-state components can then be labeled in terms of donor states. Although almost certainly not point defects, the energy states are characterized by Γ_i, the irreducible representations of the T_d site symmetry of a conventional donor.[22] This characterization is used because of the donorlike behavior of the IBE. Thus, with FIEAS information available, the two lowest PL transitions (S_B^0 and S_B^1 for S_B, and S_A^0 and S_A^1 for S_A) are identified with the donor Γ_1 ground state.

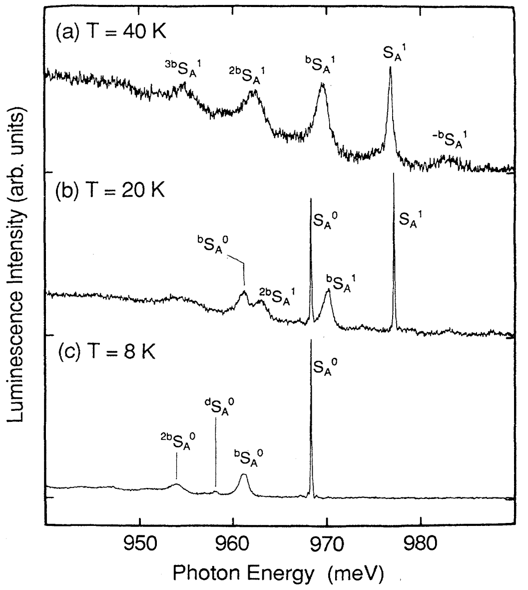

FIG. 3. High-resolution photoluminescence spectra of the S_A system as in Fig. 2.

The solitary NP S_B^0 transition shown at 8 K in Fig. 2(c) quickly loses strength to S_B^1 in the higher-temperature spectra of Figs. 2(b) and 2(a). The low oscillator strength of the lowest-lying ground (S_B^0) state is common for IBE's in which electron-hole (*e-h*) *j-j* coupling is important.[3] This *e-h* *j-j* coupling in the reduced symmetry of the defect often results in the observation of three $1s\Gamma_1$ ground-state components, the lowest of which is dipole forbidden. The splitting of the ground state by the *e-h* coupling and the crystal field is discussed in detail by Dean and Herbert,[3] and by Monemar *et al.*[4] The PLE results, discussed later, reveal evidence of a third component of this $1s\Gamma_1$ state, which we label S_B^2.

The corresponding spectra for S_A are shown in Fig. 3. The strong similarities between the two systems are obvious. The same low oscillator strength is observed for the lowest-lying ground state and the splitting of the two lowest states is again large, although not quite as great as that for the more tightly bound S_B system. Evidence of a third component, S_A^2, corresponding to S_B^2, will again be presented with the PLE results. A list of the NP transition energies for both systems is given in Table I.

Although only two local modes are evident in the S_A system, they correspond closely to the *b* and *d* phonons observed in S_B. The correspondence between the *d* phonons in the S_A and S_B systems is exact both in energy and width as far as can be determined. The *b* phonon replica in the S_B system has a sharp feature at 6.7 meV, similar in energy to the *b* phonon replicas in the S_A system which are broad and centered at 7.1 meV. The energies of the local-mode phonons are summarized in Table II.

B. Photoluminescence excitation spectroscopy

The strong nonresonant background as well as the phonon-assisted absorption band makes the PLE spectroscopy of these centers very difficult. It is only after comparison with the much clearer FIEAS data that it becomes possible to identify the PLE transitions. The binding energies of the states responsible for the PLE transitions can be calculated from the IBE ionization energies obtained from FIEAS. These binding energies allow the identification of the transitions following Ref. 23.

TABLE I. Si:S IBE no-phonon transitions observed by photoluminescence and photoluminescence excitation.

Line Label		Energy (meV)	Wavelength (μm)
$1s\Gamma_1$	S_A^0	968.24±0.10	1.281
	S_A^1	977.05±0.10	1.269
	S_A^2	988.0±1.0	1.255
S_A: $1s\Gamma_3, 1s\Gamma_5$		1004.7±1.0	1.234
		1006.5±1.0	1.232
$1s\Gamma_1$	S_B^0	811.96±0.10	1.527
	S_B^1	821.91±0.10	1.509
	S_B^2	833.8±1.0	1.487
S_B: $1s\Gamma_3, 1s\Gamma_5$		848.3±1.0	1.462
		851.5±1.0	1.456

TABLE II. Energies of local-mode phonons observed in PL.

Phonon	Energy (meV)	Width (meV)	Observed In
a	5.4	0.3	S_B
b	6.7	0.4	S_B
	7.1	1.1	S_A
c	9.0	0.3	S_B
d	10.1	0.6	S_A,S_B

PLE spectra for both the S_A and S_B systems are shown in Fig. 4, aligned according to the energies of the lowest NP transitions seen by PL, namely S_A^0 and S_B^0. The S_A^0 and S_B^0 lines are not observed in PLE due to their low oscillator strengths. In the higher-energy system, Fig. 4(a), a strong excitation is present at 977 meV. This corresponds exactly with the S_A^1 NP line seen in PL at temperatures $T \geq 15$ K and identified as a splitting of the IBE ground state. At least three higher-lying phonon replicas of the S_A^0 absorption spaced at ~7-meV intervals are clearly visible. These correspond to the *b* phonon energy observed in PL for the S_A system.

The next no-phonon structure which is observed at higher energy in Fig. 4(a) is the shoulder at 988 meV on the $^{-2b}S_A^1$ phonon replica. There are $-b$, $-2b$, and $-3b$, phonon replicas of this shoulder, and, as mentioned previously, it is identified as a splitting of the $1s\Gamma_1$ IBE

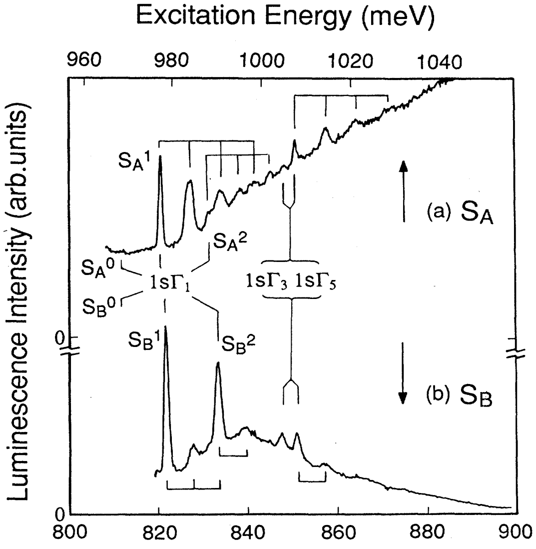

FIG. 4. Photoluminescence-excitation spectra of the S_A and S_B systems, shifted so as to align S_A^0 with S_B^0. The multielement brackets over many of the lines indicate phonon replicas in the PLE spectrum, where the leftmost element in each series is the no-phonon transition.

ground state and is thus labeled S_A^2.

Moving up in energy, there is a fairly strong excitation at 1006.5 meV, again with multiple *b*-type phonon replicas. Based on its position relative to the odd-parity states found in FIR-BE absorption, it can be identified with the $1s\Gamma_3$ or $1s\Gamma_5$ valley-orbit-split states of the ground-state manifold. There is also a small transition at 1004.7 meV which we interpret as the other $1s\Gamma_3$ or $1s\Gamma_5$ ground-state component. The large valley-orbit splitting of the 1*s* ground state indicates that the central-cell potential, which tightly localizes the hole of the IBE, is also attractive for the electron. This is also consistent with the large size of the *e-h j-j* coupling, as seen previously for the Si:In IBE[24]

Consider now the PLE spectrum shown in Fig. 4(b) of the lower-energy S_B system. A structure very similar to that of the S_A system is evident. Again the strongest feature is the excitation of the S_B^1 ground-state NP transition at 821.9 meV, with at least one *b*-type phonon replica spaced at ~6 meV. The second phonon replica, $^{-2b}S_B^1$, at 833.8 meV is superimposed on a no-phonon transition, S_B^2, explained as the same splitting of the $1s\Gamma_1$ state labeled S_A^2 in the higher-energy system. Also present at 848.3 and 851.5 meV are the $1s\Gamma_3$ and $1s\Gamma_5$ states along with their weak phonon replicas. The NP transition energies observed in PLE are also included in Table II.

All of the PLE structure presented here has been attributed to various splittings of the IBE ground state. No true excited states (i.e., $n > 1$) were observed. Without an independent method of determining the IBE binding energy and levels of the higher states, the structure observed by PLE could easily have been misinterpreted as higher even-parity states, such as 2*s*. It is only by using FIEAS that the given ground-state labelings could be made.

C. Far-infrared exciton absorption spectroscopy

In contrast to the PLE spectra, the FIR spectrum shown in Fig. 5(a) reveals a wealth of excited states and no broad background. Shown below this for comparison, on a shifted energy scale in Fig. 5(b), is the more common FIR impurity-absorption spectrum of the Si:P donor. The similarities between the two are obvious, and it is clear that the FIEAS spectrum is made up of two donorlike excited-state series, separated by 0.93 meV. The S_A IBE system is identified with the lower-energy series and S_B with the higher series by relating the behavior of the FIEAS and PL spectra as a function of excitation level and temperature, as will be discussed later. It is important to note that in the absence of excitation, the absorption lines attributed to S_A and S_B were not detectable,

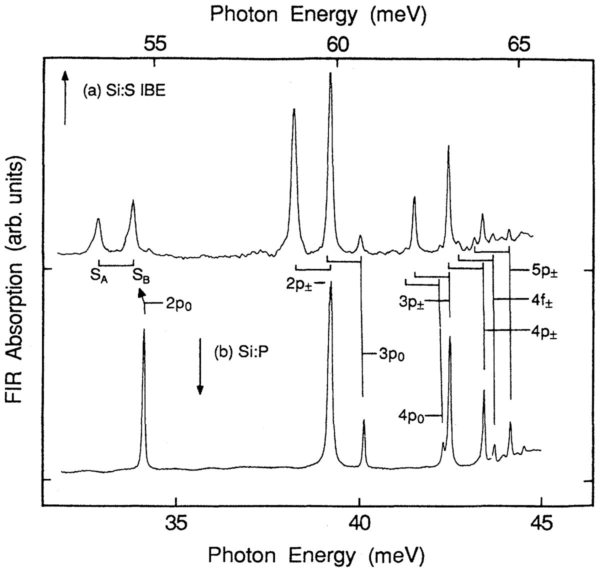

FIG. 5. The photoinduced Si:S bound-exciton infrared absorption (top) is compared to the shifted P-donor absorption spectrum (bottom). The top spectrum consists of two donorlike series, split by 0.93 meV, which arise from the S_A and S_B IBE ground-state to excited-state transitions.

TABLE III. Electron binding energies of Si:S IBE (meV).

	S_A IBE[a]		Comparison[b]	
Level	S_A	S_B	Si:P[a]	Theory
$1s\Gamma_1$	65.28±0.09	66.21±0.09		
	56.47±0.17	56.26±0.17	45.59	
	45.52±0.17	44.37±0.17		31.27
$1s\Gamma_5$	28.8±1.1	29.9±1.1	33.89	
$1s\Gamma_3$	27.0±1.1	26.7±1.1	32.58	
$2p_0$	11.78±0.17	12.75±0.17	11.48	11.51
$2p_\pm$	6.44±0.17	6.37±0.17	6.40	6.40
$3p_0$	5.44±0.17	5.57±0.17	5.47	5.48
$4p_0$	3.39±0.17	3.36±0.17	3.31	3.33
$3p_\pm$	3.12	3.12	3.12	3.12
$4p_\pm$	2.22±0.17	2.22±0.17	2.19	2.19
$4f_\pm$	1.95±0.17	1.92±0.17	1.90	1.89
$5p_\pm$	1.50±0.17	1.50±0.17	1.46	1.44

[a] Obtained by defining the $3p_\pm$ binding energy to be equal to the theoretical value of 3.12 meV (Ref. 23).

[b] After Ref. 22 and references therein.

even though the material is *n*-type and impurity absorption due to the shallower phosphorus donor was present. This confirms that the FIEAS transitions are due to BE and not to two new donors.

Using Faulkner's value of 3.12 meV for the binding energy of the $3p_{\pm}$ state,[23] electron binding energies of 65.3 meV for S_A and 66.2 meV for S_B are obtained. These energies are unexpectedly large, more than twice the effective-mass value, again indicating an electron-attractive central-cell potential. The binding energies of all the states found in PL, PLE, and FIEAS are summarized in Table III along with the corresponding values for the P donor and from effective-mass theory.

The binding energies of the isolated holes on these isoelectronic centers can in turn be obtained by subtracting the electron binding energy within the IBE from the total IBE binding energy for each of the two systems. This gives hole binding energies of 135.7 meV for S_A and 291 meV for S_B.

In order to relate each FIEAS series to its PL counterpart it is necessary to compare their behavior under a variety of conditions. This was accomplished by investigating their dependence on temperature and excitation level. The FIEAS spectra are summarized in Fig. 6, with the spectrum of Fig. 6(b) serving as a reference for the other two, which show the effect of increased excitation level, Fig. 6(a), and increased temperature, Fig. 6(c).

With increasing temperature, the induced absorption of both systems should decrease as the higher-energy component of the ground state becomes thermally populated, thereby reducing the population of the longer-lived, lowest-energy state from which the FIEAS transitions originate. This behavior is observed and the rate at which S_A^0 and S_B^0 depopulate is consistent with the relative decrease in induced absorption of the two systems as shown in figs. 6(b) and 6(c). Comparison of these spectra shows that the induced absorption of the S_A system decreases much faster with increasing temperature than that of S_B. Inspection of the S_A^0 and S_B^0 PL transitions under similar conditions reveals that the depopulation of S_A^0 into S_A^1 occurs more quickly than that of S_B^0 into S_B^1.

In general, the induced absorption of the S_A IBE was observed to increase more strongly with increasing excitation level than that of the S_B IBE. In Fig. 6(a), the excitation level has been increased by a factor of 4 from a starting point of approximately 30 W/cm^2, Fig. 6(b). There is very little, if any, effect on the S_B system, but the induced absorption of the S_A system is doubled. The same general behavior is observed for the PL intensities. In particular, for a change in incident intensity similar to that in Figs. 6(a) and 6(b), the PL intensity of S_A^0 also doubles, whereas there is only a slight increase for S_B^0, confirming the correspondence made between the FIEAS and PL results.

It was first thought this correspondence between the FIEAS and PL could be conclusively made by switching to the 1.32-μm line of the Nd:YAG laser. Since this is lower in energy than the S_A ground state, efficient creation of S_A IBE's was not expected to occur and the resulting FIEAS spectrum would therefore show only the S_B IBE ground-state to excited-state transitions. Both series of absorption lines, however, remained with the

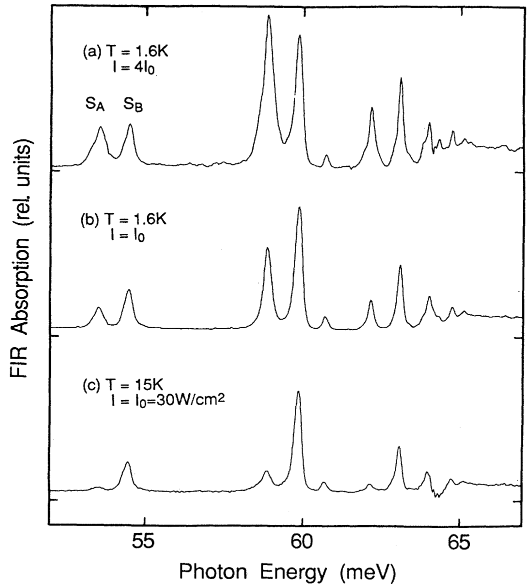

FIG. 6. The temperature and excitation-level dependences of the FIEAS results are shown. The middle spectrum serves as a reference for the top spectrum, increased excitation, and for the bottom spectrum, increased temperature.

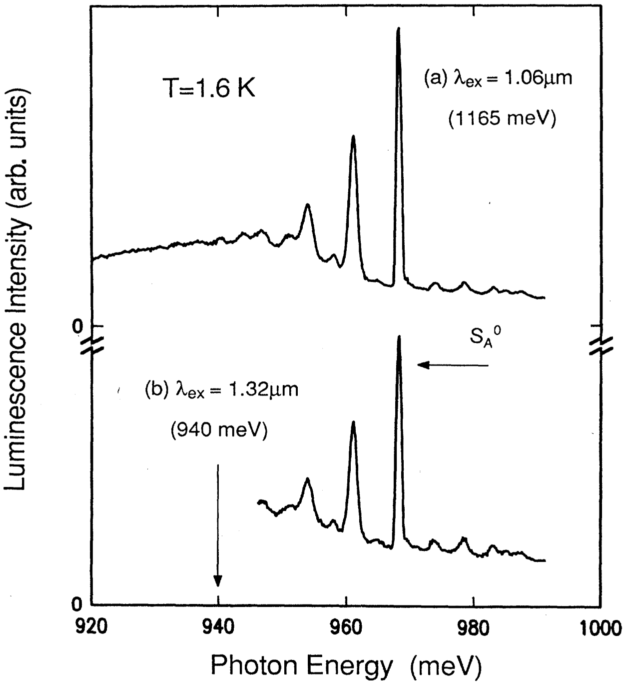

FIG. 7. The photoluminescence of the S_A system with excitation at (a) 1.06 μm, higher in energy than the no-phonon S_A^0 transition, and (b) 1.32 μm, below the no-phonon transition as shown by the arrow.

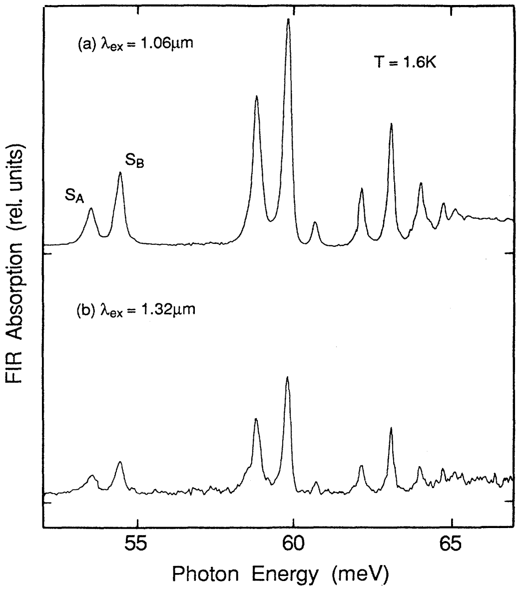

FIG. 8. The FIEAS results for excitation at (a) 1.06 μm and (b) 1.32 μm.

1.32-μm excitation. This unexpected result led to PL measurements with 1.32-μm excitation, in which the S_A IBE PL was found to be efficiently produced, as shown in Fig. 7, even though the excitation photons are of longer wavelength than the PL photons. The S_A^0 line and its phonon replicas produced with the 1.06-μm excitation are shown in Fig. 7(a), and the same system produced with the 1.32-μm excitation is shown in Fig. 7(b).

FIEAS spectra showing the effects of the two excitation wavelengths are shown in Fig. 8. The 1.32-μm induced absorption for both the S_A and S_B systems, Fig. 8(a), is approximately half that of the 1.06-μm induced absorption, Fig. 8(a). This ratio is similar to that observed for PL. The relatively low continuous-wave excitation-power levels used here preclude any simultaneous two-photon absorption process, so the effect must result from some form of two-step absorption process involving a long-lived intermediate state. The fact that both systems are affected suggest that the S_B IBE could be an intermediate step in the up-conversion production of the S_A IBE. However, preliminary measurements made with the OPO show that the S_A luminescence still persists even at excitation energies as low as 775 meV, well below the lowest S_B NP energy of 812 meV.

IV. SUMMARY AND CONCLUSIONS

We have applied photoluminescence, photoluminescence excitation, and far-infrared exciton-absorption spectroscopies to two recently discovered centers in Si doped with S. These centers, which we have called S_A for the 968-meV system and S_B for the 812-meV system, exhibit strikingly similar properties with all three techniques.

The lowest NP transitions (i.e., IBE ground state to crystal ground state) were found using high-resolution, low-temperature PL. Higher energy components of the IBE ground states were found using PLE, but no true excited states were observed with this method. The electronic excited-state structure of both systems, observed using FIEAS, was identified as being donorlike with electron binding energies of 65.3 and 66.2 meV for the S_A and S_B systems, respectively. These values indicate an unusual binding center in that its central-cell potential is attractive for both holes and electrons. Another unusual feature is the ability to efficiently produce the S_A IBE PL with excitation below the lowest S_A NP transition energy.

The presence of both the S_A and S_B systems in all samples, as well as the mentioned similarities, suggest that the binding centers themselves must be very similar, differing perhaps only in the configurations of the constituents, similar to the bistable Tl-related IBE in Si.[25] In addition, these centers provide an excellent example of the utility of the new FIEAS technique, especially in cases where the PLE spectrum is obscured by nonresonant processes. However, much more work needs to be done in order to determine the chemical details of the binding centers.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We are also grateful for financial support from NSERC, the British Columbia Advanced Systems Foundation, and Simon Fraser University.

---

[1] M. Lampert, Phys. Rev. Lett. **1**, 450 (1958).

[2] J. R. Haynes, Phys. Rev. Lett. **4**, 361 (1961).

[3] P. J. Dean and D. C. Herbert, in *Excitons,* Vol. 14 of *Topics in Current Physics,* edited by K. Cho (Springer-Verlag, Berlin, 1979), p. 5555.

[4] B. Monemar, U. Lindefelt, and W. M. Chen, Physica B+C **146B**, 256 (1987).

[5] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[6] J. W. Allen, J. Phys. C **4**, 1936 (1971).

[7] A. Baldereschi, J. Lumin. **7**, 79 (1973).

[8] There are many examples of the use of this technique. Two of the earliest are R. A. Faulkner and P. J. Dean, J. Lumin. **1/2**, 552 (1970), and E. Cohen and M. D. Sturge, Phys. Rev. B **15**, 1039 (1977).

[9] D. Labrie, T. Timusk, and M. L. W. Thewalt, Phys. Rev. Lett. **52**, 81 (1984).

[10] M. L. W. Thewalt, D. Labrie, and T. Timusk, Solid State Commun. **53**, 1049 (1985).

[11] D. Labrie, I. J. Booth, S. P. Watkins, and M. L. W. Thewalt,

Solid State Commun. **63**, 115 (1987).

[12] D. Labrie, M. L. W. Thewalt, B. P. Clayman, and T. Timusk, Phys. Rev. B **32**, 5514 (1985).

[13] T. G. Brown and D. G. Hall, Appl. Phys. Lett. **49**, 245 (1986).

[14] T. G. Brown, P. L. Bradfield, and D. G. Hall, Appl. Phys. Lett. **51**, 1585 (1987).

[15] D. G. Hall, Computer **20**(12), 25 (1987).

[16] M. L. W. Thewalt, M. Nissen, D. J. S. Beckett, and S. Charbonneau, in *Proceedings of the 3rd International Conference on Shallow Impurities in Semiconductors,* edited by B. Monemar (IOP, Bristol, 1989), Vol. 95, p. 505.

[17] M. L. W. Thewalt, U. O. Ziemelis, and R. R. Parsons, Solid State Commun. **39**, 27 (1981).

[18] J. Weber, R. Sauer, and P. Wagner, J. Lumin. **24/25**, 155 (1981).

[19] M. L. W. Thewalt, U. O. Ziemelis, S. P. Watkins, and R. R. Parsons, Can. J. Phys. **60**, 1691 (1981).

[20] S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981), p. 68.

[21] M. L. W. Thewalt and D. J. S. Beckett, Can. J. Phys. **66**, 868 (1988).

[22] A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981).

[23] R. A. Faulkner, Phys. Rev. **184**, 713 (1969).

[24] S. P. Watkins and M. L. W. Thewalt, Phys. Rev. B **34**, 2598 (1986).

[25] S. P. Watkins, M. L. W. Thewalt, and T. Steiner, Phys. Rev. B **29**, 5727 (1984).