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Absorption due to Bound Excitons in Silicon

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Measurements have been made on the weak, but sharp, absorption bands due to the creation of excitons bound to neutral donor and acceptor centers in silicon, including a no-phonon component and a momentum-conserving phonon-assisted component involving transverse optical phonons. The oscillator strength of these transitions increases roughly in proportion to the relative strength of the no-phonon components in the spectra from different donors and acceptors, and is approximately 5× larger for the acceptors than for the donors. A splitting observed only for the acceptor-exciton complexes is interpreted by differences in the electrostatic interaction between the $J=0$ and $J=2$ states formed from the two $j=\frac{3}{2}$ holes by j-j coupling. The observed magnitude of this splitting is proportional to the localization energy of the bound exciton and therfore to the ionization energy of the acceptor. Absorption due to transitions assisted by transverse acoustical phonons has also been detected for some of the acceptor-exciton complexes. The relative intensities of the momentum-conserving phonon replicas in absorption, where measurable, are in good agreement with the bound-exciton luminescence spectra. A weak-absorption step attributed to the no-phonon creation of free excitons in the vicinity of the impurity atoms has been observed for the bismuth donor and gallium acceptor in silicon.

I. INTRODUCTION

In 1958 Lampert proposed that stable complexes involving, among other possibilities, excitons bound to neutral donor or acceptor centers should occur in semiconductors.[1] Experimental proof of such complexes was first obtained in 1960 by Haynes,[2] who observed sharp lines close to the exciton energy gap in low-temperature luminescence spectra of silicon consistent with the radiative decay of excitons bound to a variety of donor and acceptor centers.

Since then, luminescence due to the decay of excitons bound to shallow donor and/or acceptor centers has been observed from a wide variety of semiconductors, notably in germanium,[3] silicon carbide,[4] diamond,[5] and gallium phosphide.[6] Of these indirect gap materials, the bound-exciton complexes have so far only been reported in absorption for gallium phosphide.[7,8]

This paper describes absorption due to excitons bound to neutral donors and acceptors in silicon. The no-phonon components are unambiguously identified from a comparison of the transition energies in the absorption and luminescence spectra. The oscillator strengths of the bound-exciton transitions measured from the absorption spectrum increase roughly in proportion to the relative strength of the no-phonon components, as expected since the detectable phonon-assisted components involve only those phonons which conserve momentum for the indirect transitions. The oscillator strengths of these momentum-conserving phonon-assisted components for excitons bound to neutral acceptors are about 5× larger than for excitons bound to neutral donors, independent of the donor or acceptor. Like the intrinsic exciton transitions at the indirect energy gap in silicon, the transverse optical (TO) phonon predominates in the phonon-assisted bound-exciton transitions involving shallow donors and acceptors. The relative strength of the no-phonon and phonon-assisted transitions is similar in the absorption and luminescence spectra. The absorption spectra were measured with greater spectral resolution than has been possible in luminescence, and two no-phonon components were resolved for the acceptor complexes. These components arise from the two states, $J=0$ and $J=2$, constructed from the spin-spin interaction between two $j=\frac{3}{2}$ holes. The energy difference between these two states is approximately proportional to the ionization energy of the acceptor.

II. EXPERIMENTAL

Czochralski-grown silicon single crystals containing $\sim 10^{17}$ cm^{-3} donor or acceptor centers were used. Parallelopiped samples of dimension 2.0 cm ×0.7 cm ×0.3 cm were cut from these ingots, and were mounted for transmission measurements with the light incident on a 0.7 cm×0.3 cm face. Light from the tungsten-iodine source was passed through a gallium arsenide filter and focused onto the sample in a conventional helium immersion Dewar. The transmitted light was focused onto the entrance slit of a Perkin-Elmer model 112 spectrometer equipped with a Bausch and Lomb 1200 line/mm grating and a lead sulphide photodetector cooled with dry ice. The infrared radiation was chopped at 25 cps and the signal was detected using standard

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[1] M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).

[2] J. R. Haynes, Phys. Rev. Letters 4, 361 (1960).

[3] C. Benoit á la Guillaume and O. Parodi, in *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 426.

[4] For results on cubic silicon carbide see W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. 133, A1163 (1964).

[5] P. J. Dean, E. C. Lightowlers, and D. R. Wight, Phys. Rev. 140, A352 (1965).

[6] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. 131, 2397 (1963).

[7] M. Gershenzon, D. G. Thomas, and R. E. Dietz, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1962), p. 752.

[8] P. J. Dean, Phys. Rev. 157, 655 (1967).

TABLE I. Parameters of the absorption components due to the formation of excitons bound to neutral donors and acceptors in silicon.

Impurity	Electrical behavior and concentration (cm^{-3})	No-phonon transition Energy, eV[a]	Half-height bandwidth ΔE, meV[b]	I^0/I^{TO}	Total oscillator strength[c]	Oscillator strength of TO phonon replica[c]
Antimony	Donor, 6.0×10^{16}	1.2083–0.0580	0.55	<0.1	$\sim7\times10^{-6}$	$\sim7\times10^{-6}$
Phosphorus	Donor, 1.3×10^{17}	1.1501	0.55	0.3	7.1×10^{-6}	5.3×10^{-6}
Arsenic	Donor, 2.5×10^{17}	1.1492	0.70	0.8	1.0×10^{-5}	5.6×10^{-6}
Bismuth	Donor, 2.3×10^{16}	1.1472	0.55	?	2.2×10^{-5}	6.9×10^{-6}
Boron	Acceptor, 3.6×10^{17}	1.1503; 1.1512	1.3[d]	?	2.9×10^{-5}	2.8×10^{-5}
Aluminum	Acceptor, 1.8×10^{17}	1.1492; 1.1505	1.0	0.25	3.7×10^{-5}	2.9×10^{-5}
Gallium	Acceptor, 4.0×10^{17}	1.1490; 1.1505	1.9	0.3	4.1×10^{-5}	3.2×10^{-5}
Indium	Acceptor, 2.3×10^{16}	1.1410; 1.1441	1.4	>3	1.1×10^{-4}	2.3×10^{-5}

[a] Maximum error ±0.2 meV, energy splitting for acceptors also accurate to ±0.2 meV.
[b] Maximum error ~±10%.
[c] Maximum error ~±20%.
[d] Measured for the higher-energy absorption band, the (weaker) lower-energy band is significantly broader.

lock-in techniques and displayed on a chart recorder. The spectra were recorded with the helium pumped below the λ point to minimize light scattering in the Dewar.

III. RESULTS AND DISCUSSION

The bound-exciton absorption in silicon due to $\sim10^{17}$ cm^{-3} donor or acceptor centers is very weak. The decrease in transmission at the center of the no-phonon line was generally $\lesssim10\%$, even for a 2-cm pathlength. Higher impurity concentrations were not used because of line broadening due to interactions between adjacent impurities. Split no-phonon (Al_1^0 and Al_2^0) and TO phonon-assisted (Al_1^{TO} and Al_2^{TO}) components can be clearly seen in the transmission spectrum from an aluminum-doped crystal shown in Fig. 1. The no-phonon resonance transitions are so identified from the equality, as near as can be determined, of the energies in column 3 of Table I with the energies of the highest-energy bound-exciton components observed in luminescence.[2,9] The aluminum spectrum is a typical in that weak-absorption replicas involving the transverse acoustical (TA) momentum-conserving phonons can also be seen. The intensity ratio Al_2^0/Al_2^{TA} is about 3:1 in Fig. 1, in good agreement with the luminescence of excitons bound to aluminum acceptors.[9] The TA replicas were also detected for boron and gallium acceptors, but not for any of the available crystals containing other donors or acceptors. The intensity ratio B^{TA}/B^{TO}, measured in absorption, was ~5.5%, also in good agreement with the estimate obtained from the luminescence spectrum of excitons bound to boron acceptors.

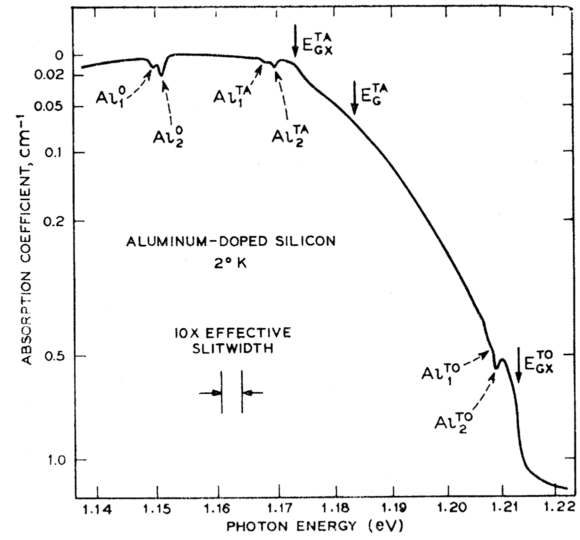

FIG. 1. Transmission spectrum of 2.0-cm-thick silicon crystal containing 1.8×10^{17} cm^{-3} aluminum acceptors showing the sharp absorption lines due to zero-phonon (Al_1^0 and Al_2^0) and phonon-assisted (Al_1^{TA}, Al_2^{TA}, Al_1^{TO}, and Al_2^{TO}) transitions. The arrows labeled E_{GX}^{TA} and E_{GX}^{TO} denote the principal thresholds of intrinsic absorption due to the creation of triplet state free excitons with the emission of the same momentum-conserving phonons as occur in the bound-exciton transitions. Free electron-hole pairs are produced by photoexcitation above E_G^{TA}. The splitting of the bound-exciton absorption lines is due to hole *j-j* coupling within the neutral acceptor-exciton complex (see text).

The oscillator strengths f of the bound-exciton transitions were calculated from the absorption spectra using the relationship

$$Nf=0.97\times10^{16}n\alpha_{\max}\Delta E, \tag{1}$$

where N is the concentration of impurity centers[10] (cm^{-3}), n is the refractive index (3.7 for silicon), $\alpha_{\max}$(cm^{-1}) is the peak absorption coefficient of the absorption band, and ΔE(eV) is the half-height bandwidth. Equation (1) is the form of the Smakula relationship applicable to an inhomogeneously broadened[11] transition associated with diffuse impurity states in a

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[9] P. J. Dean, J. R. Haynes, and W. F. Flood (unpublished).

[10] N was estimated from four-probe measurements of the room-temperature resistivity using the data of J. C. Irvin [Bell System Tech. J. 41, 387 (1962)] assuming that all the conductivity in these essentially uncompensated crystals was due to carriers thermally released from the relevant substitutional impurity (see Ref. 13).

[11] It is argued below that inhomogeneous internal strain contributes significantly to the breadth of these absorption lines, so the relationship appropriate to a Gaussian line has been used in Eq. (1).

semiconductor. It is believed that local field corrections can be omitted in this relationship if, as for these weakly bound-exciton complexes, the radii of the electronic states are greatly in excess of the interatomic separation in the crystal.[12,13]

The absorption components due to phonon-assisted transitions must be included in Eq. (1) together with the no-phonon component. Only the TO-phonon-assisted bound-exciton transition is significant in silicon (Fig. 1), and it was directly measured in absorption for many impurities. The intensity ratios, I_0/I_{TO}, of the no-phonon and TO-phonon-assisted components, where measurable (Table I), were consistent with corresponding ratios obtained from the luminescence spectra,[9] as is also true for the momentum-conserving phonon replicas in the absorption and luminescence of excitons bound to neutral donors in gallium phosphide.[8] The luminescence values of I_0/I_{TO} were therefore used in the derivation of the oscillator strengths for the bismuth and indium exciton complexes, since the TO-phonon-assisted absorption components were too weak to be accurately measured for these impurities. The oscillator strengths of the TO-phonon-assisted components were therefore also derived and are included in Table I.

Table I shows that the total oscillator strengths of the bound-exciton transitions increase with the ionization energy of the impurity,[14] and therefore, with decrease in the transition energy.[15] As near as can be determined, the oscillator strengths of the TO momentum-conserving components are independent of the particular donor or acceptor center, however. This is as expected, since a significant increase in the strength of the phonon-assisted components caused by the increased impurity-exciton interaction for the deeper donors and acceptors should involve phonons of arbitrary wave vector. The increase in the exciton-phonon interaction for the deeper centers is evidenced by the increase in the oscillator strength of the no-phonon transitions as well as by the increasing exciton localization energies. Only the momentum-conserving phonons can be detected in the bound-exciton spectra, however. These components arise from transitions in which the effect of the impurity center on the matrix element for the exciton-phonon interaction is negligible.[16]

The oscillator strengths f_A for the acceptor momentum-conserving phonon-assisted transitions in Table I are uniformly higher than for the corresponding donor exciton transitions f_D, the mean ratio being ~5:1. This difference in oscillator strength may be due to the difference in degeneracy of the donor and acceptor-bound-exciton complexes and, in addition, may indicate that intermediate states in the conduction and valence bands may contribute differently to indirect bound-exciton transitions at donor and acceptor centers.[16] According to this difference in oscillator strengths, the radiative decay times of the shallow acceptor-exciton complexes should be only ~20% of the shallow donor-exciton complex decay times. The measured decay times τ_A and τ_D of the luminescence of these four particle bound-exciton complexes is governed by the relatively efficient (nonradiative) Auger decay process, however, whereby the transition energy of the recombining bound exciton is entirely given up to the second electron or hole which is ejected deep into the conduction or valence band.[17] The decay time has only been measured for the arsenic donor complex, (80 nsec), but is probably similar for the other donors. The relative probabilities of the Auger and radiative decay processes for the acceptor and donor complexes may be different, although the similarity of the luminescence efficienties of these two types of complex suggests that this difference is not large. It is therefore unlikely that the experimental lifetime ratio τ_D/τ_A for the bound-exciton luminescence will be simply related to f_A/f_D, as would be expected if the Auger decay process was not predominant.

The principal features of the absorption spectrum associated with donor-exciton complexes are two relatively sharp lines associated with the no-phonon and TO-phonon-assisted transitions. The TO-phonon energy, determined from the energy separation of these lines, is 58.0±0.2 meV, in good agreement with the bound-exciton luminescence spectra.[2,9] The TA momentum-conserving phonon energy estimated from bound-

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[12] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 363.

[13] Note that an incorrect form of Eq. 1 was inadvertently used in a recent paper on bound-exciton transitions in gallium phosphide (Ref. 8). The local-field term was incorrectly factored out of the right-hand side of Eq. (4) in Ref. 8, which should be multiplied by $\frac{1}{9}$. The estimates of oscillator strength of the bound-exciton transitions in gallium phosphide derived from this equation should therefore be reduced by the same factor. These corrected oscillator strengths are two to three orders of magnitude less than for excitons bound to isoelectronic nitrogen centers in gallium phosphide. These larger differences between the oscillator strengths are more consistent with the marked differences in the form and relative magnitude of the phonon coupling exhibited by the two different kinds of exciton complex in gallium phosphide (Ref. 25).

[14] The intensity ratio I_0/I_{TO} varies considerably among the donors and acceptors in silicon (Table I and Ref. 9). A simple view of the bound-exciton transitions in an indirect gap material (Ref. 8) holds that the oscillator strengths of the momentum-conserving phonon replicas will be constant independent of the impurity for sufficiently weakly bound states. The integrated oscillator strength for the transition would therefore be expected to increase with the ratio I_0/I_{TO}. The results of Table I are consistent with this prediction.

[15] It has been shown in Ref. 2 that the localization energy E_{Bx} of the bound exciton is approximately proportional to the ionization energies of the donor or acceptor centers.

[16] It is shown in Ref. 9 that the ratio of the coupling to the TA and TO momentum-conserving phonons is slightly but significantly greater for the bound exciton compared with the free-exciton recombinations in silicon, and that this difference increases with increase in the localization energy of the bound exciton. Thus, the matrix elements for these phonon-assisted bound-exciton transitions are not precisely determined from the free-exciton transitions. The difference may be connected with the local stress induced by the impurity atom, since it is greater for the larger impurity atoms and the relative strength of the TA free-exciton luminescence component increases significantly under uniaxial stress.

[17] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters 17, 1262 (1966).

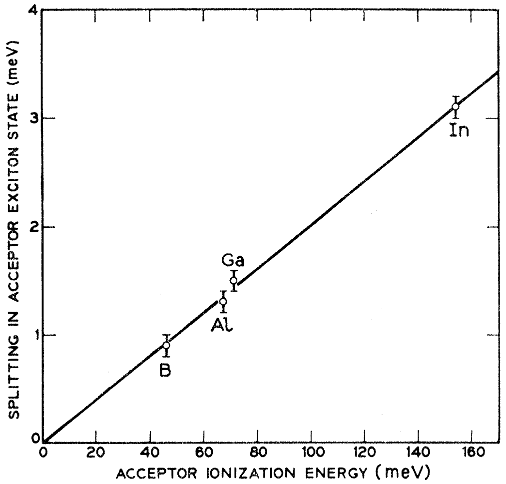

FIG. 2. The energy separation between the $J=0$ and $J=2$ hole states in several neutral acceptor-exciton complexes in silicon as a function of the ionization energy of the acceptors.

exciton absorption spectra for several acceptors (18.4±0.1 meV) is also in agreement with the luminescence data. Two subcomponents can be resolved in the corresponding transitions for each of the acceptor-exciton complexes, however, (Table I and Fig. 1). This splitting was not observed in luminescence because of inadequate spectral resolution.[18] The relative intensity of the two subcomponents is not very dependent upon the acceptor center,[19] although the energy separation varies from 0.9 meV for boron to 3.1 meV for indium. Since the spectra were recorded at ~2°K, this suggests that the two components arise from a splitting in the excited state of the transition. No splitting is in fact anticipated in the ground state of this exciton transition.

In the acceptor-exciton complex, the electron is bound to the negative acceptor ion by a hole pair bond. This excited state can split because of the different electrostatic interaction between the holes in the two stable configurations ($J=0$ and $J=2$) constructed on the $j-j$ coupling scheme using two $j=\frac{3}{2}$ holes from the Γ_{8+} valence-band maximum.[20] The Γ_{7+} valence band, split off by spin-orbit interaction, can be neglected in these considerations since the $\Gamma_{8+}-\Gamma_{7+}$ splitting (38 meV)[21] is much larger than the localization energies ($\lesssim 14$ meV) of excitons at these acceptor centers. The higher-energy components ($Al_2{}^0$ and $Al_2{}^{TO}$ in Fig. 1) should correspond to the singlet hole state, where the interaction between the two holes is greatest. This structure is only observable in semiconductors which crystallize with cubic structures, since the degeneracy of the upper valence band is lifted by the crystal field in hexagonal crystals. Only the singlet state is possible for the electron pair bond constructed from two $j=\frac{1}{2}$ electrons in the donor-exciton complex, even for cubic semiconductors.

The splitting between the $J=0$ and $J=2$ hole states should increase in proportion to the strength of the hole pair bond, and therefore to the localization energy E_{Bx} of the bound exciton. Figure 2 shows that the observed splitting increases linearly with the ionization energy E_A of the acceptor center, as expected from the above remarks.[15]

An additional possible source of splitting in these bound-exciton complexes arises from $J-j$ interaction between the quintuplet hole state and the $j=\frac{1}{2}$ electron, producing two states with $J=\frac{5}{2}$ and $J=\frac{3}{2}$. The magnitude of this splitting should be of the order of the splitting recently observed by the present authors between the $J=1$ and $J=2$ states of the free exciton in silicon, which is 1.7±0.1 meV. This splitting should not depend strongly upon the ionization energy of the acceptor. No such splitting was resolved in the present work. It is possible that the transition to the $J=\frac{5}{2}$ state is too weak to be observed in these absorption measurements, since the strength of the transition to the $J=2$ free exciton state is only ~13% of that to the $J=1$ state.

At a given impurity concentration, the half-height bandwidths of the acceptor-bound-exciton absorption lines appreciably exceed those of the donor-exciton lines, and the acceptor-exciton absorption lines are also significantly broader for the larger, relatively insoluble, impurities bismuth and indium (Table I). These impurities exhibit large values of E_{Bx},[2] which implies that the wave functions of the corresponding bound-exciton states are relatively compact. It is therefore unlikely that the larger values of ΔE are produced by concentration broadening associated with wave function overlap between adjacent acceptor centers. Inhomogeneous broadening caused by the strain introduced directly by the substitutional impurities probably makes a significant contribution to the linewidths, particularly for those heavier impurities which are relatively close to the solubility limit at the concentrations quoted in Table I. The hole states in weakly bound-exciton complexes closely follow the splitting of the Γ_{8+} valence band induced by shear strain.[22] Since it is unlikely that indium and gallium substituents, respectively, induce more long-range lattice strain per atom than bismuth and arsenic, the larger value of ΔE must be due either to

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[18] The luminescence transition energies for acceptor-exciton complexes given in Ref. 9 are in fact weighted towards the lower-energy component in Table I because of thermal quenching of the upper state at 30°K.

[19] The intensity ratios $Ga_2{}^0/Ga_1{}^0$ and $Al_2{}^0/Al_1{}^0$ (Fig. 1) are both ~2:1, but $In_2{}^0/In_1{}^0$~1:1.

[20] A recently reported splitting of the *ground state* of neutral mercury double acceptors in germanium has been similarly interpreted. R. A. Chapman W. G. Hutchinson, and T. L. Estle, Phys. Rev. Letters **17**, 132 (1966).

[21] T. Staflin, J. Phys. Chem. Solids **27**, 65 (1966).

[22] This has been confirmed experimentally for excitons bound to shallow donors and isoelectronic centers in gallium phosphide by I. Balslev [J. Phys. Soc. Japan, Suppl. **21** (1966)] and independently by the present authors.

the presence of *two* holes in the acceptor-exciton complexes or to a greater strain introduced by the acceptor impurities during crystal growth.

It is interesting to note that the values of ΔE associated with the donor-exciton complexes (Table I) are comparable with those reported at low temperature by Colbow for individual lines in the photoexcitation spectra of boron acceptors and attributed to concentration broadening,[23] in spite of the $\sim 10\times$ larger impurity concentrations used in the present work. This apparent discrepancy may be connected with the great disparity between the oscillator strengths for the interbound state impurity transitions and the exciton transitions (ratio $\sim 10^4{:}1$) since the concentration broadening in the former has been attributed to interactions between excited acceptor states.[23]

In addition to the sharp bound-exciton absorption lines, weak continuous absorption with low-energy threshold near the indirect exciton energy gap E_{gx} has been resolved for bismuth donors. The additional absorption is of the form expected for the indirect parity-allowed creation of free excitons,[24] that is the absorption coefficient increases as $(h\nu - E_{gx})^{1/2}$ as near as can be determined for this weak absorption. Absorption processes of this type can occur in the absence of a Coulomb interaction between the exciton and impurity center, and arise from the no-phonon creation of free excitons at impurity atoms. Such absorption processes are possible since the exciton can interact with the strain field around the substitutional impurity. Bound-exciton transitions may occur in addition at isoelectronic impurities, depending sensitively upon the magnitude of this interaction.[25] The nophonon free exciton band introduced in silicon by only 2.3×10^{16} cm^{-3} bismuth impurities is surprisingly strong, about 20% of the strength of the TA-phonon-assisted intrinsic components. The no-phonon absorption process is expected to be most prominent for relatively insoluble substitutional impurities which strain the lattice. The magnitude of the chemical shift in the ionization energy of the donor is related to these effects, and is exceptionally large for bismuth donors in silicon.[26]

A similar component was also observed in the spectra of excitons bound to gallium acceptors, but the available indium-doped crystal was not of sufficient optical quality to enable the presence of very weak absorption steps to be established.

IV. SUMMARY

The integrated absorption associated with the creation of excitons bound to neutral acceptors in silicon is very weak but is $\sim 5\times$ stronger than the corresponding absorption involving donor centers. The ratio of recombination lifetimes for donor- and acceptor-exciton complexes is not expected to correspond precisely to the oscillator strength ratio determined from absorption measurements, since the recombination process is dominated by Auger transitions. A qualitative comparison of the luminescence efficiency of these complexes suggests that the deviation produced by the Auger process is probably quite small, however. No-phonon, TA- and TO-phonon-assisted transitions occur with impurity-dependent relative strengths consistent, where comparison is possible, with previous estimates obtained from the luminescence of these complexes. Additional phonon-assisted transitions observed in luminescence are too weak to be detected in absorption. A weak-absorption component due to the no-phonon creation of free excitons has been detected for the bismuth donor and gallium acceptor. The greater spectral resolution possible in absorption reveals that the transitions at the acceptor-exciton complexes are split, unlike those at the donor-exciton complexes. This splitting is attributed to j-j coupling between the two $j=\frac{3}{2}$ holes in the acceptor-exciton complexes, and its magnitude is proportional both to the localization energy of the exciton and to the ionization energy of the acceptor center. Inhomogeneous strain broadening induced by the impurities appears to make an important contribution to the breadths of these bound-exciton transitions.

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[23] K. Colbow, Can. J. Phys. **41**, 1801 (1963).

[24] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[25] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[26] H. J. Horostowski and R. H. Kaiser, J. Phys. Chem. Solids **4**, 315 (1958).