VALLEY-ORBIT SPLITTING OF FREE EXCITONS? THE ABSORPTION EDGE OF Si

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Measurements of the wavelength derivative of the indirect absorption edge in Si show features associated with the creation of free excitons in states $n=1$ and 2 as well as in the exciton continuum. The spectrum shows no valley-orbit splitting of the excitons, contrary to previous suggestions, and it is shown theoretically that such splitting of free excitons cannot exist. It is found also that previous determinations of the energies of higher exciton states ($n>1$) were in error. Finally, LO phonon participation has been identified for the first time in the indirect edge of Si.

We have studied the indirect-exciton absorption edge of Si at 1.8°K using a sensitive wavelength-derivative absorption (WDA) spectrometer.[1] Although the ordinary absorption spectrum of Si had been previously measured quite thoroughly,[2] such spectra lack the sensitivity needed for direct analysis. The added sensitivity of the WDA technique has enabled us to resolve exciton transitions involving three different phonons (TA, LO, TO), whereas only two (TA, TO) had been reported previously.[2,3] Furthermore, in the present work, the $n=2$ exciton excited state and the onset of the exciton continuum are observed directly for the first time. Previously these states had been incorrectly located by numerical fitting of the ordinary absorption spectrum to the theory. On the basis of this new experimental information the following points can be made: (1) Our data show that Dean, Yafet, and Haynes[3] have incorrectly interpreted a closely spaced doublet in the luminescence and absorption spectra as valley-orbit splitting of the exciton ground state. This type of splitting had been originally suggested earlier by Ascarelli[4] for excitons in AgBr. It will be shown below that the translational invariance of the free exciton precludes the existence of valley-orbit splitting. (2) The two features of the above-mentioned doublet are shown to be due to the formation of the exciton ground state with the emission of closely spaced LO and TO phonons, respectively. This is the first identification of the LO-assisted process. (3) The measured exciton Rydberg is 14.7 meV. This value is about 50% larger than estimates based on previous experimental data[2] and now agrees quite well with the theoretical predictions of McLean and Loudon.[5]

In Fig. 1, the solid curve shows the derivative spectrum of the absorption coefficient $[d\alpha/d(h\nu)]$ obtained directly using a WDA spectrometer. The sample was immersed in liquid helium at 1.8°K. The dashed line shows, for comparison, a typical ordinary absorption spectrum of Si.[3] The arrows labeled E_2^{TA}, E_1^{TO}, and E_2^{TO} indicate structure observed directly by Dean et al.[3] The remaining downward-pointing arrows locate structure identified only through a curve-fitting procedure.[3] Note that these latter arrows do not consistently correspond to any structure in the derivative spectrum (solid line). Figure 2 shows the main features of the derivative spectrum on an expanded scale. Features in the derivative spectrum have been identified by the subscripted letters A, B, and C, and numerical values of energies are listed in Table I. The A structures (upper energy scale) have been shifted and plotted above the C structures (lower energy scale) to illustrate the similarities. Note that peaks

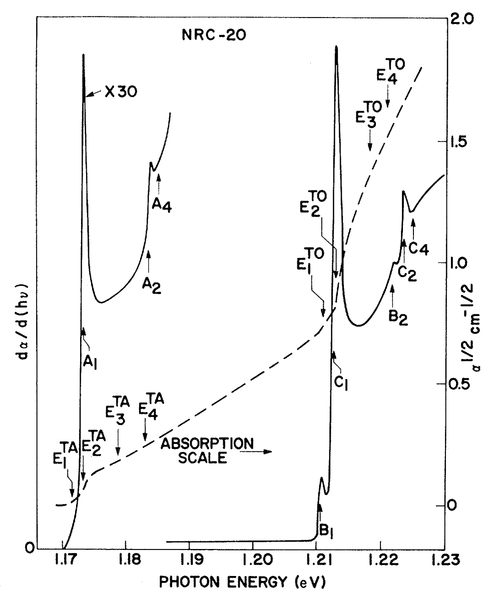

FIG. 1. Comparison of the ordinary absorption spectrum (dashed curve) and the derivative absorption spectrum (solid curve) at the indirect gap of Si at 1.8°K. The arrows with subscripted letters A_1, B_1, C_1, etc. identify features seen in the derivative spectrum, and arrows with notations E_1^{TA}, etc., were those given for the ordinary spectrum by Dean *et al.* (Ref. 3).

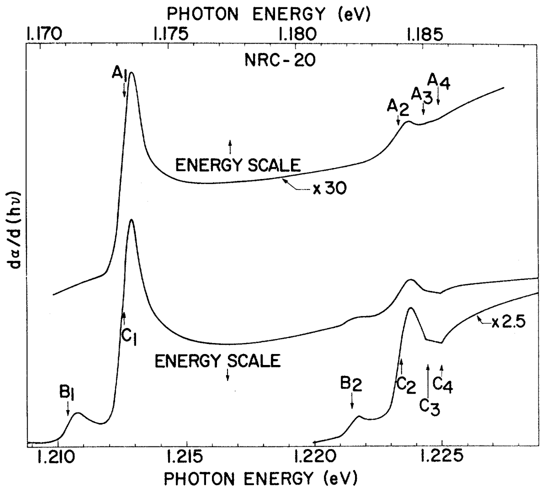

FIG. 2. The measured derivative absorption spectrum in detail for Si at 1.8°K near the indirect gap. The upper curve, which goes with the upper energy scale, has been shifted and offset for comparison with the lower curves, which correspond to the lower energy scale. The curve in the lower right hand corner is a 2.5× enhancement of this portion of the curve immediately above it. The features identified by subscripted letters on the curves result from formation of various states of the exciton with simultaneous emission of phonons as described in Table I.

subscripted 1 and 2 have the shape of a broadened square-root singularity characteristic of the formation of an allowed indirect exciton.[6,7] These peaks are well resolved with a signal-to-noise ratio better than 50:1, whereas the corresponding structure in the ordinary absorption spectrum appears only as a change in slope (E_2^{TO} in Fig. 1 for example).

Following McLean,[2] the A_1 structure has been interpreted as the formation of a ground-state indirect exciton accompanied by the emission of a TA phonon. At 77°K, processes involving both emission and absorption of TA phonons can be observed. From this spectrum we deduce an energy of 18.2 ± 0.2 meV for the TA phonon, a value in good agreement with previous reports.[2] Using this we obtain the exciton energy gap and subsequently other phonon energies. The TA phonon-assisted transition has been reported to be a doublet by Dean et al.[3] (E_1^{TA} and E_2^{TA} in Fig. 1) with a 1.8 meV separation and an intensity ratio of 7:1. No such doublet is seen in the derivative spectrum near A_1 in Fig. 2. We shall make use of this observation later.

The B_1 and C_1 structures (Fig. 2) are attributed to the formation of a ground-state exciton accompanied by the emission of a 55.3 meV LO phonon and a 57.3 meV TO phonon, respectively.

Table I. Energies and assignments of the exciton features in the derivative spectrum of Si at 1.8°K. Phonon energies obtained are $E^{\mathrm{TA}} = 18.2 \pm 0.2$ meV, $E^{\mathrm{LO}} = 55.3 \pm 0.4$ meV, $E^{\mathrm{TO}} = 57.3 \pm 0.4$ meV. The exciton Rydberg is found to be 14.7 ± 0.4 meV. Because of broadening, the resonance energy for each exciton-phonon pair lies slightly to the left of the corresponding peak in the spectrum. Accordingly, the energy of each singularity (third column), except for continuum thresholds, was taken on the low-energy side of each peak at 70% of the peak amplitude. Uncertainty is estimated to be ± 0.0002 eV.

IDENTIFICATION	ENERGY OF PEAK (eV)	ENERGY OF SINGULARITY (eV)	ASSIGNMENT
A_1	1.1736	1.1733	$E_{ex}(n=1)$+TA
A_2	1.1842	1.1840	$E_{ex}(n=2)$+TA
A_4	1.1858[a]	1.1858	$E_{ex}(n\geq 3)$+TA
B_1	1.2107	1.2104	$E_{ex}(n=1)$+LO
C_1	1.2128	1.2124	$E_{ex}(n=1)$+TO
B_2	1.2217	1.2214	$E_{ex}(n=2)$+LO
C_2	1.2238	1.2234	$E_{ex}(n=2)$+TO
C_3	1.2243[a]	1.2243	?
C_4	1.2250[a]	1.2250	$E_{ex}(n\geq 3)$+TO

[a]Threshold energy.

The TO energy is in good agreement with the phonon energy obtained previously from ordinary absorption spectra.[2] All three phonon energies reported here are consistent with values obtained from neutron-scattering data[8] and from tunneling data.[9-12] The assignment of B_1 as a LO-phonon-assisted transition can be further justified by considering alternative interpretations. The most likely alternative is that the degeneracy of the exciton ground state has been lifted by some perturbation. The B_1-C_1 doublet could then be interpreted as due to the formation of different levels of the exciton ground state with the emission of only TO phonons. However, such an interpretation can be ruled out on the basis of uniaxial stress measurements and additional structure in the spectrum in Fig. 2 (details given below).

The A_2, B_2, and C_2 structures are attributed to the formation of the $n=2$ exciton excited state with the emission of TA, LO, and TO phonons, respectively. This interpretation is supported by the following observations. The A_1-A_2, B_1-B_2, and C_1-C_2 separations are all equal to within experimental uncertainty and the ratio of the ground state to the excited state intensities is 6:1 in all three cases. We expect, on the basis of effective-mass theory, that the exciton excited states should form a hydrogenic series. Assuming this, and using the energies of the $n=1$ and $n=2$ exciton states as determined from say C_1 and C_2, we find that the $n=3$ state (with emission of a TO phonon) should be at 1.225 eV, very close to C_4. Hopfield[13] has pointed out that broadening can cause the higher-lying excited states to merge. It can then be shown that the absorption coefficient for energies above the state at which merging occurs (say the nth state) is proportional to $(E-E_n)^{3/2}$, and further, that this merging tends to reduce any structure which would otherwise have appeared at the usual continuum ($n=\infty$).[7] Thus the threshold C_4 (also A_4) is attributed to the onset of transitions into the merged exciton states $n\geq 3$ with the emission of a TO (TA) phonon. We can then calculate, on the basis of a hydrogenic series, an exciton Rydberg of $R=14.7 \pm 0.4$ meV. This value agrees quite well with the effective-mass calculations of McLean and Loudon[5] who found $12.0<R<14.5$ meV. On the basis of this model, it appears that the central cell shift of the exciton ground state is small.

I has previously been suggested by Dean et al.[3] that the B_1-C_1 splitting was due to valley-orbit splitting of the ground state of the indirect exciton. This interpretation is inconsistent with the above data for the following reasons: (1) A splitting of the exciton implies that the TA phonon-assisted transition (A_1) should be a doublet with the same separation as the B_1-C_1 doublet. The A_1 structure in Fig. 2 is however only a singlet. (2) The B_2-C_2 doublet due to the exciton excited state has the same separation as B_1-C_1, but valley-orbit splitting (central-cell correction) of an excited state should be significantly less than that of the ground state. (3) We find that a uniaxial stress along the (111) direction, which lifts the conduction-band degeneracy, causes identical splitting of B_1 and C_1. If the B_1-C_1 doublet were a consequence of the valley-orbit interaction, then a (111) stress should change the B_1-C_1 separation, but no such change is observed. (4) The doublet in the luminescence spectra of Dean et al.[3] is the mirror image of the B_1-C_1 doublet in Fig. 2, supporting the assignment of two different phonons. These results show that valley-orbit splitting of the free exciton is not observed. In fact, any existing splittings of the exciton states must be less than the experimental resolution (0.5 meV).

It can further be shown theoretically that valley-orbit splitting of free excitons, an idea originally advanced by Ascarelli,[4] cannot exist. This is so because of the translational invariance of the exciton Hamiltonian.[13] The result can readily be seen by considering the matrix elements of the perturbation Hamiltonian H_1 describing the electron-hole interaction,

$$H_{ij}=\langle\psi_i{}^*|H_1|\psi_j\rangle,$$

where H_1 is translationally invariant, and ψ_i and ψ_j are the exciton wave functions for the ith and jth branches of the star of exciton crystal momentum $\vec{K}$. Applying the translation operator T to H_1, we can write

$$H_{ij}=\langle\psi_i{}^*|T^{-1}TH_1|\psi_j\rangle=e^{i(\vec{K}_i-\vec{K}_j)\cdot\vec{a}}H_{ij},$$

where $\vec{a}$ is a lattice vector. This latter relation is satisfied only if

$$H_{ij}=0 \text{ for } i\neq j,$$

since no two different conduction-band valleys can be connected by a reciprocal lattice vector. There are no off-diagonal matrix elements to mix the different exciton states on the star of K; therefore, valley-orbit splitting of free excitons cannot exist.

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$$\alpha(h\nu)\sim[h\nu-\epsilon_g+\epsilon_{ex}(\vec{K}_0,n)-\hbar\omega_{\vec{K}_0}]^{1/2},$$

where $\vec{K}_0$ is the center-of-mass momentum of the exciton, $h\nu$ is the photon energy, ϵ_g is the band gap, and $\hbar\omega_{\vec{K}_0}$ is the energy of the momentum-conserving phonon (only phonon emission is considered). The absorption coefficient associated with the exciton continuum has

the form

$$\alpha(h\nu) \sim [h\nu - \epsilon_g - \hbar\omega_{\vec{K}_0}]^{3/2}.$$

In the derivative technique the exponents of the arguments of α become $-\frac{1}{2}$ and $\frac{1}{2}$, respectively.

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[10]Measurements of the second derivative of the tunneling current in a Si diode gave $53.2 < E^{\mathrm{LO}} < 55.4$ meV and $56.5 < E^{\mathrm{TO}} < 58.7$ meV (Ref. 9). Neutron-scattering data (Ref. 8) give similar phonon energies, assuming that the conduction-band minima lie at $\vec{k}_0 = 0.85\, \vec{k}_{\mathrm{max}}(100)$ (Ref. 11). Recent ENDOR measurements in Si (Ref. 12) indicate an uncertainty possibly as large as ±15% in this value of k_0. Thus the neutron-scattering data are consistent with a TO-LO energy difference as small as 1 meV.

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[13]We are indebted to J. J. Hopfield for pointing out the importance of the translational invariance of the free exciton Hamiltonian and the merging of the higher-lying exciton excited states.

INSENSITIVITY TO COSMIC RAYS OF THE GRAVITY RADIATION DETECTOR*

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A search for coincidences between cosmic-ray shower signals in a large scintillation counter and gravitational-radiation detector signals indicates that the gravitational radiation detector does not produce a signal when hit by showers of particle density of the order of 100 particles/m^2.

The inherent interest in and significance of the reported discovery of gravitational radiation[1] calls for establishing the certainty of these results. It has been suggested that some of the signals in the gravitational radiation detector could be due to the deposition of energy in the large aluminum cylinder used as a detector.[2] It might also be possible for cosmic radiation to excite the piezoelectric crystals used to couple the normal mode of cylinder oscillations to the electromagnetic degree of freedom of the detector. We monitored cosmic rays at a gravitational radiation detector, and the coincidence rate between cosmic ray events and excitations of the detector was found to be consistent with the rate for accidentals. The experiment showed no evidence for sensitivity of the gravitational radiation detector to cosmic-ray events corresponding to more than 100 particles/m^2 recorded by the scintillator telescope. Details of the experimental arrangement and the results obtained are presented below.

Two large ($27 \times 36 \times \frac{1}{2}$ in.) plastic scintillators[3] in a telescope arrangement were placed immediately over the 96-cm.-diam gravitational-radiation detector. The scintillators were centered over the piezoelectric crystals and covered approximately 0.45 of the length of the detector. The detector has been previously described in Ref. 1. Each scintillator was viewed by two 7746 photomultiplier tubes attached by a light piping arrangement which covered an entire 27-in. $\times \frac{1}{2}$-in. edge. For each scintillator the signals were fed into an "or" circuit and the outputs of the two circuits were put into coincidence. This coincidence pulse was used to gate a linear gate and stretcher which stretched the summed outputs of all four photomultipliers. A threshold detector in the form of an integral discriminator on the output of the linear gate and stretcher was used to produce a marker pulse which was stretched to about $\frac{1}{4}$ sec and recorded on a chart recorder. This chart could be read to about 0.1 min. The output of the gravitational-radiation detector was also recorded on a chart recorder. Figure 1 shows a block diagram of the electronics with pertinent pulse widths indicated.

The scintillation detectors were calibrated using a radioactive gamma-ray source to relate signal size to energy deposition. It was observed that a Co^{60} source (which deposited a maximum of 2.5 MeV in the two detectors when one decay gamma ray from each decay went into the detectors) gave a signal of a certain maximum amplitude at the output of the linear gate and stretcher. In the experimental run the photomultipliers were operated at lower voltage to avoid any saturation problem. Using the published gain versus applied voltage characteristics[4] of the photomultiplier, as well as the relative attenuator settings, we then evaluated the energy deposition from a shower, assuming that all the particles