Magnetic perturbations of excitons bound to an isoelectronic hydrogen-related defect in silicon

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It is shown that recent data on the optical properties of the B^1_{71} (1.1377 eV) hydrogen-related defect in silicon can be fitted using a physically simple model in which the excited states are constructed from the band extrema of silicon. The model describes the energy levels of the center, the relative intensities of the transitions, and the effects of magnetic fields up to 12 T. The center lies in the limit of weak binding of the known "singlet/triplet" isoelectronic systems in silicon.

Hydrogen is well known as a passivator of unsatisfied chemical bonds in imperfect crystals.[1] The rate of diffusion of hydrogen through a crystal and its total concentration in the crystal are affected by the presence of traps for the hydrogen. Possible traps include impurities, dislocations, and radiation damage centres. Recently, several photoluminescence centers produced by radiation damage of silicon have been shown to involve hydrogen,[2] and so are of considerable interest not only in their own right but also as traps and storage points for the hydrogen.

Kaminiskii *et al.*[3] have presented a study of one of these photoluminescent traps, the B^1_{71} center. Luminescence from the center consists (at low temperature) of the X^1_{71} zero-phonon line at 1137.68 meV (9176.3 cm^{-1}) and the X^1_{68} line 0.32 meV (2.6 cm^{-1}) to higher energy (Fig. 1), plus the X^1_{60} line 1.14 meV above X^1_{71} and the X^1_{57} line 1.44 meV above X^1_{71}. A further state, from which luminescence is forbidden in the unperturbed center, lies an estimated 0.035 meV below the X^1_{71} state. As a first stage in identifying the structure of the complex, Kaminiskii *et al.*[3] have presented a very detailed study of the effects of magnetic fields of up to 12 T on the two lowest-energy optical transitions, and have established that the symmetry of the complex is C_{3v}. It is shown here that a very simple model can be used to fit their data for the zero-field energy-level structure, the relative optical transition probabilities, and the effects of magnetic fields on the energies and intensities of the lowest-energy lines. The B^1_{71} center is shown to fit into the sequence of "singlet/triplet" isoelectronic systems in silicon, but with the weakest observed exciton binding observed to date.

Kaminskii *et al.*[3] used arguments which were heavily based on symmetry considerations to describe the energy levels of the lowest states at zero field and with an applied magnetic field. Using the separations (0.035 and 0.32 meV) of the lowest-energy excited states, they obtained two parameters (which represent the internal axial field at the center and the electron-hole exchange coupling). The changes in energy of the lowest lines produced by magnetic fields were fitted accurately when the hole g factors for the field parallel and perpendicular to the trigonal axis were taken as further adjustable parameters.

An alternative analysis, and one with a considerably simpler physical basis, is to represent the excited states of the center by a hole derived from the valence-band maxima at $\mathbf{k}=\mathbf{0}$, plus an electron in the A_1 valley-orbit state. By considering these states explicitly, we can use their known properties to minimize the number of adjustable parameters used to describe the bound exciton. The local trigonal field of the center may have symmetry-lowering elements, which split the hole states, and symmetry-conserving elements, which simply shift the origin of the energy scale. Since the excited state of the X^1_{71} line indicates an exciton binding energy (relative to the free exciton) of only 17 meV, we will first ignore the splitoff $j=\frac{1}{2}$ valence-band states and use only the $j=\frac{3}{2}$ states. We will denote their splitting by the local axial field by $\pm p$. Additionally, the energy levels are determined by the electron-hole coupling through the exchange interaction Δ. The combined effect of p and Δ is to produce five energy levels from the $j=\frac{3}{2}$ states at energies (measured from the origin determined by the symmetry-conserving

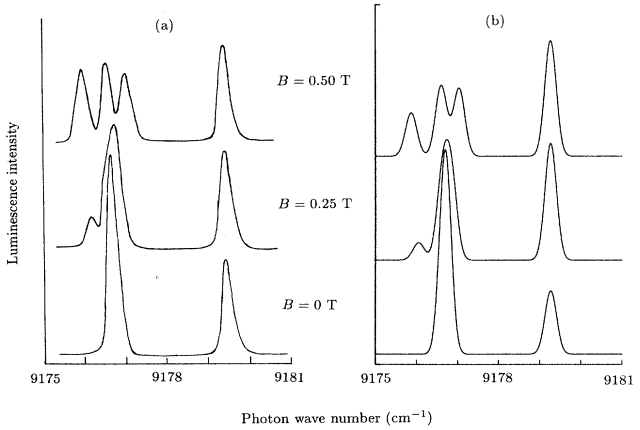

FIG. 1. (a) Spectra measured at 2 K for magnetic fields of zero, 0.25, and 0.5 T parallel to ⟨001⟩ (Ref. 3). At zero field the lower-energy transition is the X^1_{71} line and the higher energy is the X^1_{68} line. (b) Calculated unpolarized spectra for the same fields, assuming thermalization between all states at 2 K. For illustrative purposes, Lorentzian line shapes have been used in (b) with the same widths as those observed in (a).

potential) of[4]

$$\tfrac{5}{8}\Delta+p,\quad -\tfrac{3}{8}\Delta\pm p,\quad \tfrac{1}{8}\Delta\pm\tfrac{1}{2}\sqrt{\Delta^2-2\Delta p+4p^2}\ . \qquad (1)$$

A fit to the observed spacings of the four photoluminescence lines is obtained with

$$\Delta=0.40\ \text{meV and}\ p=-0.42\ \text{meV}\ . \qquad (2)$$

In the calculations,[4] p is represented by a uniaxial dilationless stress parallel to the $\langle 111\rangle$ symmetry axis of the center. The effect of a shear stress with tensor components s_{ij} (GPa) in the cubic axes x, y, z of the crystal is the splitting of the $j=\frac{3}{2}$ valence-band maximum by $\pm 53 s_{ij}$ meV,[5] so that the equivalent stress has components of only $s_{ij}=-0.008$ GPa, the negative sign indicating a compression. The hole states can be written as combinations of the P_X, P_Y, and P_Z orbital states, with the Z axis being the axis of quantization. Allowing for all the different $\langle 111\rangle$ orientations of the centers, it is easy to calculate the relative optical transition probabilities from each exciton state to the vacuum ground state *with no further adjustable parameters.* The lowest-energy electric-dipole transition represents the X^1_{71} line. The values of the two parameters, Δ and s_{ij}, in the model yield optically allowed transitions at energies 0.33 and 1.10 meV above the X^1_{71} state, compared to the measured values of 0.32 and 1.14 meV. The ratio of the transition probabilities from the X^1_{71} and the X^1_{68} lines is predicted to be 0.24, in precise agreement with experiment (Fig. 1). Additionally, a state is predicted 0.072 meV below X^1_{71}, compared to the estimated 0.035 meV, and transitions from this state are predicted to be forbidden, as observed. The calculation predicts a doubly-degenerate state 0.78 meV above X^1_{71}. Transitions from this $S=1$ state are rigorously forbidden by the spin selection rule. (Note that while optical transitions are group-theoretically allowed from the two highest-energy Γ_3 states in Fig. 1 of Ref. 3, their structure in terms of the basis states is such that electric-dipole transitions are forbidden from one pair.) The origin of the line 1.44 meV above X^1_{71} is not determined; it could be from a higher-lying electron valley-orbit state, but we have no detailed data on this line.

Turning to the magnetic field data, since the excited states are being represented by weakly trapped particles, we simply calculate the perturbations of each state in terms of the g factors of the free-electron and free-hole basis states. In contrast to Kaminskii *et al.*,[3] this approach introduces no additional adjustable parameters. The calculated perturbations are shown in Fig. 2 with the experimental data from Ref. 3. With the exception of the $\langle 110\rangle$ field, where the outer components do not shift as fast as reported, the agreement is satisfactory. Kaminskii

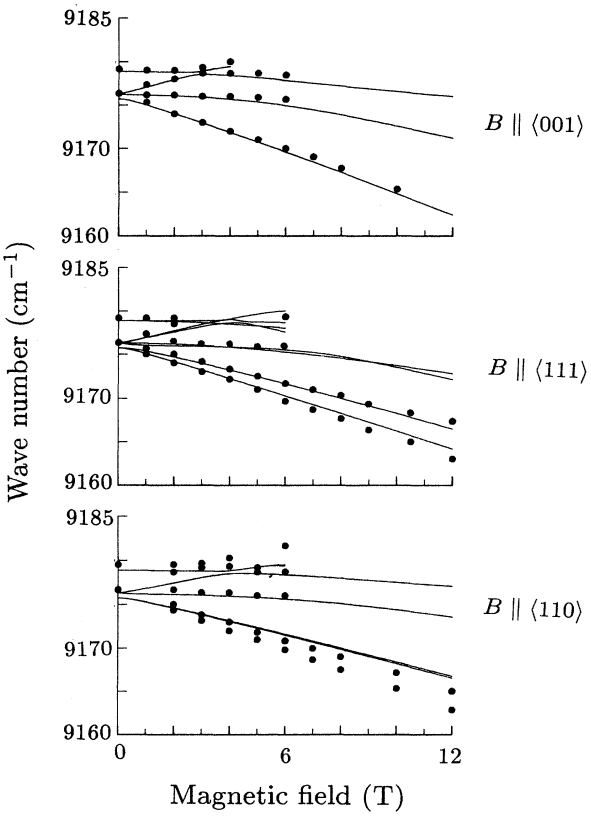

FIG. 2. Points show the energies of the lower-energy observed transitions from the B^1_{71} center measured at 2 K for magnetic fields parallel to $\langle 001\rangle$, $\langle 111\rangle$, and $\langle 110\rangle$ (Ref. 3). At zero field, the lower-energy transition is the X^1_{71} line and the higher energy is the X^1_{68} line. The lines are calculated.

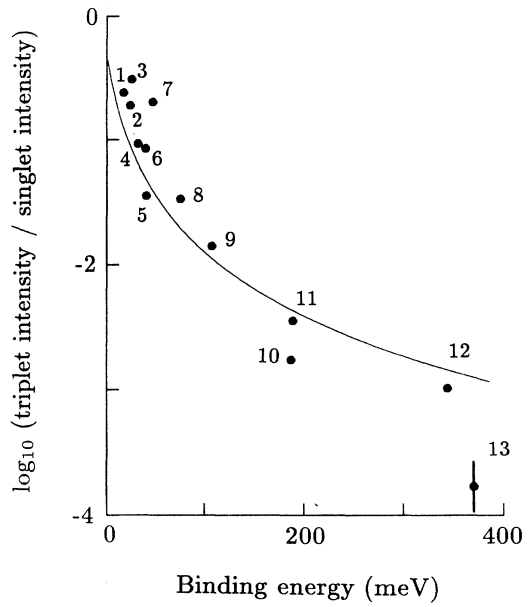

FIG. 3. Points show measured data for the ratio of the transition probabilities of known "triplet/singlet" systems in silicon as a function of their exciton binding energies. In order of increasing binding energy, the data are for (1) the X^1_{71} line (Ref. 3), (2) the Y line (Ref. 9), (3) the In-related P line (Ref. 10), (4) the Z line (Ref. 9), (5) the X^4_{05} line (Ref. 11), (6) the X line (Ref. 9), (7) the J line (Ref. 11), (8) the S line (Ref. 6), (9) the Q line (Ref. 6), (10) the S_a line (Ref. 7), (11) the Se_a line (Ref. 12), (12) the S_b line (Ref. 7), (13) the Se_b line (Ref. 12). The line is the calculated intensity ratio with the approximation that all the observed binding is produced by the local axial field.

et al.[3] drew particular attention to the effect of a ⟨001⟩ field in inducing optical transitions from the state 0.035 meV below X_{71}^{1}. The corresponding results from the calculation are shown in Fig. 1. The evolution of the spectra with increasing magnetic field is described satisfactorily with no further adjustable parameters.

These calculations show that the zero-field energies and intensities, and the effects of magnetic fields on the intensities and transition probabilities are closely reproduced by this model. The electron and hole interact through an exchange energy of $\Delta=0.4$ meV. For comparison, the lithium-related triplet-singlet system with its zero-phonon line at 1045 meV has $\Delta=1.1$ meV,[6] and the S-Cu system has $\Delta=11$ meV with zero-phonon lines near 968 meV (Ref. 7) (illustrating the tendency for Δ to increase with deeper, i.e., more localized, excited states).

At the B_{71}^{1} center, the hole is weakly trapped in the trigonal field of the defect, but the axial part of the field accounts for only 0.6 meV of the total exciton binding of 17 meV (relative to the energy of the free exciton). The negative sign of the axial field [Eq. (2)] indicates a compressive local equivalent stress. When we consider those centers with compressive local fields, we note that with increasingly large negative stress, the lowest-energy hole state tends increasingly towards a pure P_Z orbital state, as the $j=\frac{3}{2}$ and $\frac{1}{2}$ valence-band maxima are mixed. The pure P_Z state has zero orbital angular momentum. In the limit of large compressions, the lowest exciton state is a pure spin triplet, formed from the combination of the spins of the electron and hole, and electric-dipole transitions from it are forbidden. Figure 3 gathers data for the known "singlet/triplet" systems in silicon, and shows the ratio of the "triplet" to "singlet" transition probabilities as a function of the measured exciton binding energy (defined as the difference in energy between the free exciton, 1155.2 meV, and the singlet state). The line shows the calculated intensity ratio of the triplet and singlet lines for each center, *assuming that all the binding energy is produced by the perturbation by the local axial field on the hole.* We have seen that this is a poor approximation for the X_{71}^{1} line, and, in general, some of the binding is expected to be produced by a nonaxial potential (equivalent to a local hydrostatic stress) and also from the binding of the electron. Nevertheless, the datum points lie on a surprisingly uniform trend. For some of the centers (e.g., the lithium-related line at 1045 meV), the local axial field is produced by the deformation resulting from a self-trapping of the exciton,[8] for others (e.g., the S-Cu lines near 968 meV) only about half of the binding comes from the lattice relaxations and the remainder is an intrinsic axial field from the center. It remains to be seen how much of the binding of the X_{71}^{1} state is produced by a lattice relaxation; the vibronic sideband of the X_{71}^{1} line has not yet been measured, due to the weak luminescence in currently available samples. However, it should be noted that although the X_{71}^{1} line has the smallest binding energy of all the lines represented on Fig. 3, it already recognizably falls into the singlet/triplet class of bound excitons.

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