Optical properties of isoelectronic centers in crystalline silicon
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Chapter 3

Optical Properties of a Silver-Related Defect in Silicon

Doping crystalline silicon with silver results in a photoluminescence center with multiplet no-phonon structure near 778.9 meV. We show that the published assignments of the vibronic sidebands are wrong, with severe implications for the relative transition probabilities of the luminescence transitions from the excited states. At low temperature, most of the luminescence intensity derives from the phonon sideband associated with a forbidden no-phonon line through the phonon-assisted coupling of two of the excited states of the center. The effective mass of the vibration is determined from isotope effects to be close to the mass of one Ag atom. Uniaxial stress and magnetic perturbations establish that the current assignment of the electronic structure of the center is incorrect and that it is best described by a new variant on the “pseudodonor” model. An electron orbits in an effective $T_d$ environment, with an orbital triplet as its lowest-energy state, giving a $j = 3/2$ electron state. A tightly bound hole has its orbital angular momentum quenched by the $C_{3v}$ symmetry of the center, leaving only spin angular momentum ($s = 1/2$). These particles couple to give $J = 2, 1, 0$ states. Using this model, the temperature dependence of both the total luminescence intensity and measured radiative decay time can be understood. These data allow an estimate to be made of the thermally induced transition rate of the electron from the effective-mass excited states into the conduction band.

3.1 Introduction

It is well established that the photoluminescence (PL) of many optical centers in crystalline silicon can be described in terms of the recombination of an electron and a hole at an electrically neutral center. Usually, one of these particles is
tightly bound and the other is loosely bound. With increasing temperature, the luminescence from the centers is always quenched. However, within this generic model there is considerable diversity. The activation energy for the luminescence quenching may be equal to the binding energy of the loosely bound particle (e.g., the well-known 1014-meV Cu-related luminescence [9]), that of the tightly bound particle (e.g., the 968-meV Cu-S center [10]), that of the binding energy of the exciton to the center (e.g., the I$_2$ boron-related center [11]), or it may equal the binding energy of the free exciton (e.g., the W center [4]). The tightly bound particle may be the electron, with the loosely bound hole maintaining its orbital angular momentum, but being split into a doublet of nearly equal transition strengths (e.g., the 935-meV C-related center [12]). Alternatively, the hole may be tightly bound, quenching its orbital angular momentum and leading to a singlet, spin-triplet, spin-singlet states (e.g., the Q Li-related center [13]) with a doublet no-phonon structure of one almost forbidden line and one allowed transition. The relative strengths of transitions from these “triplet” and “singlet” states can be predicted simply from the effect on the valence-band maxima of the field binding the hole [14]. In all these cases the lowest-energy electron state is an $A_1$ state derived from the conduction-band minima.

Many centers can be produced by doping crystalline silicon with silver, as shown by Refs. [15–24] and the work cited therein. Electrical properties of silver in silicon were extensively studied and a number of Ag-related deep levels have been reported [15,16]. In a deep level transient spectroscopy (DLTS) study, Baber et al. [17] reported that silver creates an acceptor at $E_a - 0.54$ eV and a donor level at $E_d + 0.34$ eV. From the Fano structure of the ionization continuum of the center, it was deduced that the transitions occurred at a deep donor [21], later refined to be a “pseudodonor” (i.e., an electrically neutral center where an effective-mass electron can orbit in the Coulomb field of a tightly bound hole) [24]. Silver-doped silicon was also thoroughly studied by electron paramagnetic resonance (EPR); following analysis of the EPR spectra, microscopic models of several Ag-related centers were proposed [18,20].

The PL of silver-doped silicon has been investigated [21–31]. It has been found that silver doping of silicon crystals results in generation of a characteristic low-temperature emission spectrum at 780 meV [22,25,26]. In the PL spectrum narrow no-phonon lines (termed $A$, $B$, and $C$) and lower energy phonon replicas have been distinguished. The observed structure was identified as transitions from the effective-mass-like electronic states near the conduction band to the ground state. At temperatures below 8 K, the spectrum was dominated by two no-phonon lines $A$ and $B$ with energies of 778.91 and 779.85 meV, respectively [26]. Both lines produced phonon replicas with local phonon energies of approximately 6 and 15
meV. At energies of 20.7 and 33.1 meV below the $A$ line, two broad features were observed and assigned to the transverse-acoustic (TA) and longitudinal-acoustic (LA) silicon phonon replicas, respectively. At higher temperatures a third no-phonon line $C$, appeared at 784.31 meV. The intensity of this line rapidly increases with temperature while the intensities of the $A$ and $B$ lines decrease and the $A - B - C$ system thermalizes [25]. At temperatures higher than 20 K some local phonon replicas of the $C$ line were also observed.

In this Chapter we examine the multiple-excited state structure of one center. We will show that it can be described by using another variant on the bound-exciton model. The lowest-energy states consist of an effective-mass electron in a triply degenerate orbital state and a tightly bound hole. The response of the electron to external perturbations is determined by its effective $T_d$ environment, while the response of the hole is that of a nondegenerate orbital state at a center of trigonal symmetry. The low-symmetry environment of the hole quenches its orbital angular momentum, and spin-spin coupling dominates in the interaction of the electron and hole. We will show that these states interact so as to produce a very unusual vibronic structure and that the changes in luminescence intensity of the band, as functions of both temperature and secondary excitation, can be understood using the model for the electronic states.

At low temperature, most of the PL intensity derives from the phonon sideband associated with a forbidden no-phonon line (Sec. 3.3). The responses of the excited states to uniaxial stress and magnetic field perturbations are presented in Sec. 3.5. The large splitting of line $C$ under uniaxial stress establishes that the excited state should be assigned to a $T_2$ effective-mass orbital state in $T_d$ symmetry, rather than the current assignment to an $A_1$ orbital. We show that the low-symmetry environment of the hole quenches its orbital angular momentum and spin-spin coupling dominates in the interaction of the electron and hole. The mechanism through which the vibronic sideband is produced is presented in Sec. 3.6, and by using isotope data to estimate the effective mass of the vibration, it is shown to be consistent with the perturbation data. Knowing the electronic structure, the temperature dependence of both the total PL intensity and the measured radiative decay time can be understood, and we make a first estimate of the transition rate for thermal quenching of a "pseudodonor" in silicon (Sec. 3.7). We begin by presenting the experimental method and preparation of the samples.

### 3.2 Experimental details

Silver-doped silicon samples for the present study were prepared from 75-125 $\Omega$cm p-type float-zone silicon by diffusion. Thin silver layers were evaporated on both
sides of the silicon samples. The diffusion was performed for 4h at 1150 °C in a closed quartz ampoule containing 100 mbar of argon. Following the diffusion step, the samples were quenched to room temperature by dropping the whole ampoule in water. After diffusion, the surface layers were etched to remove about 70 µm in a mixture of HF and HNO₃ (1:3). For the diffusion, both natural and isotopically enriched silver (99.5 % and 99.4 % of ¹⁰⁷Ag and ¹⁰⁹Ag isotopes, respectively) was used.

The PL experiments were performed with a variable temperature continuous-flow cryostat accessing the 1.5 – 300 K range (Oxford Instruments Optistat CF). The samples were excited using a cw argon-ion laser operating at 514.5 nm. All spectra were obtained with a 1.5 m F/12 monochromator (Jobin-Yvon THR-1500) and detected by a high-sensitivity germanium detector (Edinburgh Instruments). Uniaxial stress measurements were carried out at temperatures from 4.2 up to 20 K and with stresses up to 200 MPa. For the Zeeman measurements, the magnetic field was varied from 0 up to 4.5 T.

Time-resolved measurements were carried out using a Tektronic TDS 3000 digital oscilloscope in combination with a Hamamatsu R5509-72 InP/InGaAs nitrogen-cooled photomultiplier tube. For the lifetime data of Sec. 3.7, transient excitation was achieved by using a pinhole and chopping the laser excitation beam mechanically at 200 Hz. The system response time was measured as 35 µs.

### 3.3 Structure of the luminescence band

Usually, as the temperature decreases, the no-phonon line of a band increases in intensity relative to the vibronic sideband. Figure 3.1 shows that between 25 and 1.6 K the line A weakens relative to the phonon sideband. Line A is evidently not the no-phonon line of the low-temperature band, in contrast to the assignments by Refs. [26,28]. Below 2 K a very weak line $F_0$ is resolved at 778.6 meV, 0.25 meV below A, as shown in the enlarged inset to Fig. 3.1. The ratios of the phonon sidebands $F_1$ and $F_2$ are temperature independent, Fig. 3.1, demonstrating that they derive from the same initial state. Their associated no-phonon line is established by the data in Fig. 3.2, where we show the variations with temperature of the intensity ratios of $A$ to $F_1$ and of $A$ to $F_2$. Both ratios follow Arrhenius behavior, with activation energies, respectively, of $0.26\pm0.02$ and $0.26\pm0.3$ meV, equal to the energy separations of the no-phonon lines $A$ and $F_0$. The no-phonon line associated with the sidebands $F_1$ and $F_2$ is therefore $F_0$, not the stronger $A$. Similarly, the ratio of $C$ to $F_1$ has an activation energy of 5.8±0.9 meV, equal to the spectroscopic splitting of $F_0$ and $C$ (5.7 meV). From the data in Fig. 3.2, the intensity ratio of lines $C$ and $A$ extrapolated to infinite temperature is
3.3. Structure of the luminescence band

$I_C/I_A = 21 \pm 6$, similar to the value of 28 measured directly from the ratio of $I_C/I_A$ by Iqbal et al [25]. We also agree with their result that $I_B/I_A = 0.7 \pm 0.05$.

![Diagram of PL spectra](image)

**Figure 3.1**: The upper four spectra show PL spectra of the 779-meV center in silicon measured at 1.6, 4.2, 15, and 25 K. Two one-phonon resonance modes, labeled $F_1$ and $F_2$, are observed. The no-phonon line $A$ weakens relative to $F_1$ and $F_2$ on cooling from 4.2 to 1.6 K. The inset at the top shows an enlarged (and shifted) spectrum of the $A$ and $F_0$ lines at 1.6 K. The marker is 1 meV long. The lowest curve shows the luminescence spectrum calculated as in Sec. 3.6 and for 4.2 K. The peaks are simulated using Lorentzian line shapes with the widths as determined from experiment and the intensities calculated with the parameters that give the best fit to the energy levels. In the calculation, only the $F_1$ mode has been considered. The $F_2$ mode would be produced by the same process as for $F_1$.

By extrapolating the measured ratios to infinite temperature, the total transition probabilities in the $F$ bands ($F_1 + F_2$) relative to $A$, $B$, and $C$ are

$$I_F/I_A = 0.68 \pm 0.04, \quad I_F/I_B = 1.0 \pm 0.1, \quad I_F/I_C = 0.032 \pm 0.016.$$

(3.1)
Figure 3.2: Arrhenius plots of the thermal variation of the intensities of line A relative to $F_1$ (triangles), $A$ relative to $F_2$ (squares), and $C$ relative to $F_1$ (diamonds). The activation energy for line $A$ are $\sim 0.26$ meV, equal to the spectroscopic separation of $A$ from the “forbidden” line $F_0$. The activation energy for line $C$ is $\sim 5.8$ meV, equal to the spectroscopic splitting of $F_0$ and $C$.

The phonon energies of the well-defined sidebands $F_1$ and $F_2$, measured from the no-phonon level $F_0$, are, respectively, $\hbar \omega_1 = 5.8$ meV and $\hbar \omega_2 = 14.6$ meV. The spectra of Fig. 3.1 show no discernible contributions to the sideband arising from line $B$. Lines $A$ and $F_0$ are sufficiently close that their phonon sidebands would not be separately resolved. To place an upper limit on the strength of coupling of $A$ to the 5.8-meV mode, let us suppose that the $A$ transitions contribute a fraction $f$ to the phonon sideband $F_1$, with the remainder arising from $F_0$. Then the ratio of $I_A/(1-f)I_{F_1}$ should obey a Boltzmann ratio with an activation energy equal to the separation of the lines $A$ and $F_0$. Taking account of experimental uncertainties, a maximum of 15% of the transition from level $A$ can go to the one-phonon line $F_1$, so that to a good approximation transition $A$ does not couple to one quantum of the 5.8-meV mode. The dominant luminescence at low temperature is therefore associated with an essentially forbidden line $F_0$. The peak at 767.2 meV, labeled $A^2_1$ in Fig. 3.1, is assigned to a two-phonon assisted transition of the 5.8-meV
3.4. Isotope effects

Figure 3.3: PL spectra recorded from samples doped with single isotopes of $^{107}$Ag or $^{109}$Ag. The main figure shows the effects on the lines A, B, and C in silicon doped with isotopically enriched silver (upper curves) and natural silver (lower curve). The inset shows the effect on the one-phonon lines $F_1$, $A_2^1$, and $F_2$.

mode and line A. The mechanism producing these vibronic effects is presented in Sec. 3.6.

3.4 Isotope effects

Figure 3.3 compares the high-resolution PL spectra of the 780-meV band recorded for three samples: doped with silver isotope $^{107}$Ag, silver isotope $^{109}$Ag and natural silver (52% $^{107}$Ag + 48% $^{109}$Ag). While all three spectra show a similar A – B – C structure, the linewidth for samples doped with a single silver isotope is smaller and the position of lines is shifted by $\sim 0.017$ meV for $^{107}$Ag-doped silicon and by $\sim +0.017$ meV for $^{109}$Ag-doped silicon. Also related shifts of the phonon satellites were observed. We note that the A – B – C lines in the sample containing natural silver are somewhat broader than those observed for $^{107}$Ag or $^{109}$Ag doping. The temperature dependence of the A – B – C lines in the samples doped with the monoisotopic silver was found to be in agreement with the earlier report [25]. The no-phonon shifts could be caused by different lattice strains, but taken together with the significantly greater one-phonon shifts, the data unambiguously demonstrate the presence of at least one Ag atom in the
optical center.

Isotope shifts of luminescence lines are convenient for identification of the chemical nature of such centers [9]. Heine and Henry [32] gave a quantitative description of isotope shift of no-phonon optical transitions at defects in semiconductors. If the force constant in the initial and/or final electronic state will change on isotopic substitution, an isotope splitting of the no-phonon optical transition will result. In their model, the shift of the no phonon energy $S$ is related to a softening effect of the electron and hole on the modes of the perfect lattice. When the force constants between the atoms change, the state of the electronic system alters. The effect is related to the temperature dependence of the band gap of the pure material. The presence of a carrier $c$ ($c = e$ for an electron and $c = h$ for a hole) on an atom lowers the interatomic elastic constant $A$ by a fraction $\gamma_c P_c$:

$$A' = A[1 - \gamma_c P_c]. \quad (3.2)$$

where $P_c$ is the probability of the carrier being at the impurity atom and $\gamma_c$ is the effect of the carrier.

The sum of the effects of a free $e - h$ pair $\gamma = (\gamma_e + \gamma_h)$ can be found from the temperature dependence of the band gap energy. At temperatures well above the Debye temperature this is given as [33]:

$$-\frac{dE_g}{dT} = \frac{3}{4} k(\gamma_e + \gamma_h), \quad (3.3)$$

where $T$ denotes temperature and $k$ is Boltzmann's constant. From analysis of the data for several defects, Heine and Henry concluded that

$$\gamma_h = (3.6 \pm 1.0)\gamma_e. \quad (3.4)$$

The presence of either a hole or an extra electron will soften lattice modes, the effect of a hole being significantly larger than that of an electron. The total value of the isotope shift can then be given by [32]:

$$S = \frac{2\hbar\omega_D}{5} \left( \frac{M_0}{M} \right)^{1/2} \frac{\Delta M \gamma_e}{M} \frac{\gamma}{\gamma} \left( -\frac{dE_g}{dT} \right)_{HT} P_c. \quad (3.5)$$

In Eq. 3.5 $\omega_D$ is Debye cutoff frequency, (for silicon $\hbar\omega_D = 55.6$ meV), $M_0$ is the atomic mass of a host semiconductor, $M$ is the mass of a particular impurity atom ($M \approx 108$ for silver with natural isotopic composition) and $\Delta M$ is the mass difference introduced by isotope substitution: $\Delta M = \pm 1$ for $^{109}\text{Ag}$ and $^{107}\text{Ag}$ impurities, respectively.

In order to calculate $P_c$, one must determine the wave function of the carrier bound to the defect center in either the initial or the final state (or both). Assuming
3.5. Perturbations of the no-phonon lines by magnetic and stress fields

that the 780-meV band originates from recombination at an isoelectronic center with a local hole binding potential [21], we roughly estimate the probability $P_c$ to be about 1. Further, we take $dE_g/dT$ for silicon to be $-2.1k$ at room temperature [34], and from Eq. 3.3 we have

$$\gamma_e + \gamma_h = 2.8. \quad (3.6)$$

Finally, substituting the mentioned values into Eq. 3.5 we evaluate the difference in no-point energy to be:

$$S = 0.015 \pm 0.001 \text{ meV}. \quad (3.7)$$

in good agreement with the experimentally measured value of 0.017 meV.

3.5 Perturbations of the no-phonon lines by magnetic and stress fields

The effects of magnetic fields on the lower-energy lines were measured at 4.2 and 20 K by PL (Fig. 3.4) and by optical absorption at 4.2 K for the higher-energy transitions near 796 meV (Fig. 3.5). Line C is not affected by the field. The effects of uniaxial stresses are shown for the lower-energy lines in Fig. 3.6, using luminescence at 4.2 and 20 K to enhance these low-energy transitions, and in Fig. 3.7, using absorption measurements to monitor also the higher-energy states.

The magnetic perturbations are isotropic within measuring accuracy and so contain no information about the point group of the center. This result supports the proposal that the hole is tightly bound [24], because then its orbital angular momentum is quenched, leaving only its spin angular momentum, which responds isotropically to the magnetic field at the resolution available optically.

The effects of stress are most easily seen for line C (Figs. 3.6 and 3.7). The line splits under <001> stress at the rate of $79 \pm 62$ meV/GPa, similar to the splitting of the conduction-band minima (92.5 meV/GPa. Ref. [35]). while there is little splitting under <111> stress. These results confirm the effective-mass nature of the electron. The electron state is derived from the six conduction-band minima and so transforms as $A_1$, $E$, and $T_2$ states in $T_d$ symmetry. In a basis set ordered as $A_1$, $E$, and $T_2$, $T_2^\pi$, $T_2^\sigma$, these valley orbit states are perturbed under stress...
Figure 3.4: The squares show the Zeeman effect measured for the no-phonon lines A and B, and the diamonds show transitions induced from F₀. Line C, which is not shown, does not shift, as expected from the model of Sec. 3.5. The lines are calculated as in Sec. 3.5 with parameters \( \lambda = -0.46 \text{ meV}, g_s = 1.9 \pm 0.1 \), and \( g_L = 0 \). The lines close to the data for F₀ have been obtained by downshifting the fits to the lowest-energy components of line A.

according to the symmetric matrix [36]

\[
\begin{pmatrix}
-\gamma(5 + \delta) & p s_\theta & p s_e & 0 & 0 & 0 \\
-Bs_\theta + \gamma(1 - \delta) & Bs_e & 0 & 0 & 0 & 0 \\
Bs_\theta + \gamma(1 - \delta) & C(\sqrt{3}s_e - s_\theta) & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
-C(s_\theta + \sqrt{3}s_e) & 0 & 0 & 0 & 0 & 0 \\
2C s_\theta & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

Here \( 6\gamma \) is the energy separation of the E state from the A₁ state and \( 2\delta\gamma \) is the displacement of the T₂ state from E. The terms \( s_\theta \) and \( s_e \) are the stress combinations

\[
s_\theta = 2s_{zz} - s_{xx} - s_{yy}, \quad s_e = \sqrt{3}(s_{xx} - s_{yy}),
\]

where the stress tensor components \( s_{ij} \) are written in terms of the Cartesian coordinates \( i, j = x, y, z \) of the crystal and compressive stress is defined to be positive. Hydrostatic stress terms, which would appear down the diagonal of the matrix, are omitted (and will be introduced below).
3.5. Perturbations of the no-phonon lines by magnetic and stress fields

Figure 3.5: Zeeman effect of the higher excited states, labeled as $1s(E+T_2)$ in Ref. [18], with the magnetic field along <001> and <111> directions. The squares are the experimental data, and the lines are calculated using the spin-orbit parameter $\lambda = -0.46$ meV derived from the fit of the Zeeman effect on the lines A and B (Fig. 3.4 and a spin $g$ factor $g_s = 1.3$. The line at 797.9 meV is assigned to the transition from the singlet state, analogous to line C.

An $A_1$ state is perturbed only by hydrostatic stresses and by coupling through the terms $ps_e$ and $ps_e$ to the $E$ state, Eq. 3.8. The considerable splitting of line $C$ under <001> stress and the linearity of the splitting establishes that $C$ does not have an $A_1$ state, as is central to existing descriptions of the excited states of the center [21]. Line $C$ derives from the $T_2$ component of Eq. 3.8.

Under stress, the matrix shows that the $T_2$ state splits into two components under <110> stress and is not split under <111> stress. Consequently, to obtain the two components seen in <001> stress, two in <111>, and at least three in <110> stress, the hole must not be split under <001> stress and must be perturbed into two states by <111> stress and by <110> stress. These splittings are only expected for an orbitally nondegenerate state in a trigonal local symmetry [37], which defines the environment of the hole.

Having determined the environment of the electron and hole as independent particles, we now need to consider their interaction. In an isoelectronic model, the ground state of the system is the "vacuum" state with no particles. It therefore has a spin of $S = 0$, and optical transitions are only allowed to it from the singlet
excited states. Line C is not perturbed by the magnetic fields and so has an $S = 0$ excited state. It also has a relatively high transition probability [Eq. 3.1]. The excited state of line C can be conveniently labeled $^1T_2$ in a $T_d$ notation. If the spins of the electron and hole can combine to give $S = 0$, then $S = 1$ combinations are also expected. Line A splits isotropically into five components in a magnetic field (Fig. 3.4). Borrowing atomic physics notation, a $T_2$ state has orbital angular momentum $L = 1$, which combines with $S = 1$ to give $J = 2$, 1, and 0; the $J = 2$ state would split into five components in a magnetic field, as does line A. Using a spin-orbit coupling $H_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$ and assigning the triplet state to line B predicts the $J = 0$ state 0.3 meV above B. This state can be observed in luminescence when it is induced by $<110>$ uniaxial stresses, Fig. 3.6. The same splittings are observed for the 796-meV group of lines (Fig. 3.5), and here the line ascribed to $J = 0$ can be observed at zero field at 797.2 meV. As required, it is not split by the magnetic field. The lines near 796 meV could therefore originate from the same electronic states as lines A, B, and C, with a hole state 16.9 meV higher than that involved in those lines.
3.5. Perturbations of the no-phonon lines by magnetic and stress fields

Figure 3.7: The squares show the data for the splittings of the no-phonon lines under stress along the <001>, <111>, and <110> crystal directions, measured in absorption at 4.2 K. The lines are the fits derived from the model described in Sec. 3.5.

For a more detailed description, it is convenient to write the \(^3T_2\) states in the angular momentum form

\[ |1> = (T_2^x + iT_2^y)/\sqrt{2}, \quad |0> = T_2^z, \quad |-1> = (T_2^x - iT_2^y)/\sqrt{2}. \]

The perturbation caused by the magnetic field is

\[ \Delta H_z = \mu_B (g_L L + g_S S) \cdot B. \] (3.9)

The combined stress and Zeeman perturbation matrix for the spin triplet states is given in the Appendices. The best fit to the Zeeman data for lines \(A\) and \(B\) gives \( \lambda = -0.46 \) meV, \( g_S = 1.9 \pm 0.1 \), and \( g_L = 0 \) (Fig. 3.4). Transitions induced from line \(F_0\), shown by the diamonds in Fig. 3, are described well by simply downshifting the fits to the lowest-energy components of line \(A\). The value \( g_L = 0 \) is as required for valley-orbit states. The same scheme also fits the overall splitting of the lines near 797 meV, with the same parameters \( \lambda = -0.46 \) meV and \( g_L = 0 \), but with a slightly reduced \( g_S = 1.3 \pm 0.1 \), Fig. 3.5.

To fit the stress data requires the inclusion of the hole state, moving in trigonal symmetry, with the \(C_{3v}\) point group. To define the notation we consider a particular orientation of the \(C_{3v}\) optical center with the \(C_3\) axis parallel to [111] and
with one of the reflection planes perpendicular to [110]. The hole is perturbed as

$$\Delta V_h = a_1(s_{xx} + s_{yy} + s_{zz}) + a_2(s_{yz} + s_{zx} + s_{xy}).$$  \hspace{1cm} (3.10)

where the $a_i$ are electronic operators [37]. Only two parameters $A_1$ and $A_2$ are required to describe the effect of stresses on the hole state, corresponding to the effect of each of the operators $a_1$ and $a_2$ of Eq. 3.10. From an optical transition we only measure the difference in energy between states. Consequently, we can measure the difference in their perturbations by totally symmetric stresses, but not the absolute perturbations. We therefore absorb the perturbation by hydrostatic stresses of the electron state into that of the hole state. The best fit to the effect of uniaxial stresses on the transitions $A$, $B$, and $C$ is shown by the lines in Fig. 3.6. For the singlet states, the $I_2$ level is perturbed as in Eq. 3.8. The perturbations of the optical transitions have been defined as the difference between the electron energies and the hole energies, and the compressive stress is positive. With these conventions, the best-fitting values are, with $\pm 15\%$ uncertainty, $A_1 = 6.5$ meV/GPa and $A_2 = 3.7$ meV/GPa. The one parameter for the electron state is $C = -11.2 \pm 1.5$ meV/GPa. This value is very similar to that of $-11$ meV/GPa found at the well-known 789-meV carbon-oxygen center [38] and is comparable to the free-electron parameter of $-15.4$ meV/GPa [35].

We have noted the close similarity in the no-field splitting and magnetic field perturbations of the multiplet near 796 meV and lines $A$, $B$, and $C$. The stress data for these lines can also be fitted using the same stress parameters as for $A$, $B$, and $C$. Fig. 3.7. Similarly, the higher-energy multiplet near 820 meV splits with the same shift rates as the corresponding components of line $C$ (Fig. 3.7).

The model presented here describes a considerable amount of perturbation data using an electron state derived from the $T_2$ valley-orbit states. The excited state of the line $F_0$ does not form part of this scheme. We have not been able to determine the nature of that state since the $F_0$ line is so weak. However, we note that the $E$ valley-orbit states may be expected to be of a similar energy to the $T_2$ states, and they could form the electron component of the exciton. The degeneracy $g_F$ of the triplet $E$ state would then be $g_F = 6$: its exact value is not critical in its use below in Sec. 3.7.

### 3.6 Electron-phonon coupling

The phonon sidebands $F_1$ and $F_2$ are associated with a forbidden no-phonon line $F_0$. Sec. 3.3. This situation arises when a vibration of the optical center couples the electronic state from which transitions are forbidden to one from which optical transitions are allowed. The simplest case is when the Hamiltonian of the center
contains a term that is linear in the displacement of the relevant vibrational mode. The molecular deformation produced by a vibration is expected to perturb the orbital parts of the states rather than their spins and so will only couple states of the same spin. The line $F_0$ is not readily detectable, but magnetic fields induce and shift the lower-energy components as for line $A$ (Fig. 3.4), suggesting that the excited state of $F_0$ is effectively another quintuplet. However, a definite assignment cannot be made to $F_0$ since we do not see a full Zeeman splitting, and so we will allow $F_0$ to interact with the excited states of either $A$ or $B$. However, we can exclude coupling of $F_0$ with the spin-singlet excited state of line $C$. The vibrational modes will be represented by one effective vibrational mode (with quantum energy of $\hbar \omega$). In the absence of the vibronic coupling, the states can be represented by Born-Oppenheimer products of the electronic states $\phi_X(r)(X = F, A, B)$ and the harmonic vibrational states $\chi_i(Q)$:

$$v_{X_i} = \phi_X(r)\chi_i(Q). \quad (3.11)$$

where $r$ represents the coordinates of the electrons, $Q$ is the vibrational coordinate, and $i = 1, 2, \ldots, \infty$ indicates the vibrational state. These states are coupled by an electron-phonon term $\dot{d}Q$ that is linear in the mode displacement $Q$, where $\dot{d}$ is an electronic operator. We define the strengths of these interactions as

$$c_1 = \left\langle \phi_A \left| \dot{d} \right| \phi_F \right\rangle = \left\langle \phi_F \left| \dot{d} \right| \phi_A \right\rangle, \quad (3.12a)$$

$$c_2 = \left\langle \phi_B \left| \dot{d} \right| \phi_F \right\rangle = \left\langle \phi_F \left| \dot{d} \right| \phi_B \right\rangle. \quad (3.12b)$$

Since there are negligible phonon sidebands originating from no-phonon lines $A$ and $B$, the effect of $\dot{d}Q$ on the states $\phi_A$ and $\phi_B$ themselves is approximately zero:

$$\left\langle \phi_A \left| \dot{d} \right| \phi_A \right\rangle = \left\langle \phi_B \left| \dot{d} \right| \phi_B \right\rangle = 0. \quad (3.13)$$

Similarly, we have no evidence for any phonon sidebands occurring through simple relaxation of the state $F$, and so

$$d = \left\langle \phi_F \left| \dot{d} \right| \phi_F \right\rangle = 0. \quad (3.14)$$

The state $v_{Fi}$ is mixed with $v_{Aj}$ and $v_{Bk}$ by the coupling, producing new eigenstates $\Psi_{Fp}$, $\Psi_{Aq}$, and $\Psi_{Br}$, which lie in the space spanned by $v_{Fi}$, $v_{Aj}$, and $v_{Bk}$:

$$\Psi_{X_p} = \sum_i f_{X_p} v_{Fi} + \sum_j a_{X_p} v_{Aj} + \sum_k b_{X_p} v_{Bk}. \quad (3.15)$$

The coefficients $f_{X_p}$, $a_{X_p}$, and $b_{X_p}$ may be found from the secular matrix, which has a very simple form. For each state $X = F, A$, and $B$ with the same vibrational
Figure 3.8: The energies of the lowest vibronic levels of the electronic states F, A, and B as a function of the coupling $c_1 \sqrt{\hbar/2m\omega}$, calculated with $c_2/c_1 = 0.06$. The phonon energy has been taken as 5.8 meV. The vertical dashed line shows the value of the coupling that gives the best fit to the energy separations of $F_0$, A, and B. The resulting predicted spectrum is shown by the simulated spectrum at the bottom of Fig. 3.1. The ground vibronic states are assumed to involve harmonic vibrations of the same 5.8-meV quantum.

Quantum state $p$,

$$\langle \psi_{X_p} | H | \psi_{X_p} \rangle = E^0_X + \left( \frac{1}{2} + p \right) \hbar \omega, \quad p = 0, 1, 2, \ldots, \quad (3.16)$$

where $H$ is the Hamiltonian, including the vibronic coupling, and $E^0_X$ is the energy of the (uncoupled) electronic state $X$. All the other elements of the matrix are zero except where those pairs of states are coupled by $dQ$. The effect of $\hat{d}$ on the electronic part of the Born-Oppenheimer products is defined by Eqs. 3.12a, 3.12b and 3.13. Since the coupling term $dQ$ is linear in $Q$, it only couples vibrational states that differ by $\pm 1$ in the quantum number. The coupling therefore has the form

$$\langle \psi_{F_i} | dQ | \psi_{A_j} \rangle = \langle \phi_F | d | \phi_A \rangle \langle \chi_i | Q | \chi_{i+1} \rangle$$
3.6. Electron-phonon coupling

\[ c_1 \sqrt{\frac{\hbar}{2m\omega}} \delta_{j,i+1} + c_1 \sqrt{\frac{\hbar}{2m\omega}} \delta_{j,i-1}. \]  

(3.17)

with corresponding expressions for the coupling of \( \epsilon_{F_i} \) to \( \epsilon_{E_j} \).

The eigenvalues and eigenvectors of the secular matrix can be found numerically. The variable parameters in the matrix are the differences between the three energies of the electronic states \( E^0_N \) without vibronic coupling, the coupling \( c_1/\sqrt{m\omega} \) between states \( F \) and \( A \), and the coupling \( c_2/\sqrt{m\omega} \) between \( F \) and \( B \). The measured data are the energies of the no-phonon states. \( E_F = 778.6 \) meV, \( E_A = 778.9 \) meV, and \( E_B = 779.85 \) meV, the quantum \( \hbar\omega \) (which we set equal to the quantum of the mode of \( \hbar\omega = 5.8 \) meV, since it is seen most strongly in the spectra), and the relative transition probabilities of line \( A \) to line \( F_1 \) and \( A \) to \( B \): we may also set the transition probability for the no-phonon line \( F_0 \) equal to zero. The energy levels of the lowest vibronic states are shown in Fig. 3.8 as a function of the coupling term \( c_1 \sqrt{\hbar/2m\omega} \).

It is found that a good fit can only be obtained when \( F_0 \) couples predominantly with \emph{either} state \( A \) or state \( B \). The coupling is to the state \( A \) since the two-phonon line at 767.2 meV is observable as a result of the vibronic coupling, and its energy—and also the fact that it can be observed at temperatures when the no-phonon line \( B \) is very weak (Fig. 3.1)—implies that it is produced by the \( A \) state. A least-squares fit to the data then gives

\[ c_1 \sqrt{\hbar/2m\omega} = 4.2 \text{ meV}, \quad c_2/c_1 = 0.06. \]  

(3.18)

and the energies of \( F \), \( A \), and \( B \) in the absence of vibronic coupling are obtained as \( E^0_F = 781.5 \) meV, \( E_A^0 = 782.2 \) meV, and \( E_B^0 = 779.7 \) meV.

The PL band shape, calculated for \( T = 4.2 \) K, is shown in Fig. 3.1. It is very similar to the measured spectrum with the exception that the line \( F_2 \) is omitted, since our model uses only one mode. The coupling produces a strong one-phonon transition \( F_1 \) associated with the no-phonon line \( F_0 \), but one-phonon transitions from both \( A \) and \( B \) are forbidden. The weak coupling between the states \( F \) and \( B \) leads to undetectable two-phonon transitions from the \( B \) state. The calculation shows that the phonon line at 767.2 meV (\( A_2^1 \)) reported as a local mode with energy of 12 meV [26], in fact, is produced by a two-phonon transition involving the 5.8-meV mode and occurs as a consequence of the electron–phonon coupling between states \( A \) and \( F \).

In this section we have seen that the luminescence band shape is unusual in that the phonon sidebands are not linked directly to the dominant no-phonon lines. This type of vibronic coupling appears to have been reported for only one other point defect in silicon [39]. We have shown that the spectral shape is produced by
a vibronic interaction between the lowest observed state $F_0$ and the next observed state $A$. Confirmation of the model would be provided by an independent assessment of $c_1$. From Eq. 3.18, evaluation of $c_1$ requires knowledge of the effective mass $m$ of the vibration. This information is provided by isotope doping.

With natural Ag, the modes that produce the bands $F_1$ and $F_2$ have well-defined quanta of $E_1 = 5.8$ meV and $E_2 = 14.6$ meV (Sec. 3.3). If we assume that the no-phonon level $F_0$ changes with isotopes in the same way as the closely adjacent line $A$, then the fractional changes in phonon energies are $\Delta F_1 \sim 0.012$ and $\Delta F_2 \sim 0.01$ from $^{107}$Ag to $^{109}$Ag. A very simple model of a heavy ion vibrating in a lattice shows that the frequency of vibration is approximately inversely proportional to the mass difference $\Delta M$ of the heavy (Ag) ion and the host lattice (Si) (Ref. [40]); this model provides a qualitative understanding of the resonance modes of heavy ions in diamond [41]. Applied to $^{107}$Ag and $^{109}$Ag in $^{28}$Si, it gives a fractional shift of -0.012, consistent with the observed changes.

The appropriate mass to use in evaluating $c_1$ is therefore that of the Ag atom. Then,

$$c_1 = 1.1 \times 10^{-10} \text{ J/m.} \quad (3.19)$$

Converting $c_1$ to strain,

$$c_1' = bc_1 = 0.2 \text{ eV/strain.} \quad (3.20)$$

where $b$ is the interatomic spacing of the Si crystal (0.234 nm). Strain parameters in silicon are typically of the order of 1 eV/strain, confirming that $c_1$ has a sensible order of magnitude. The line $F_0$ is induced by stresses applied along the $<111>$ and $<110>$ directions, but not the $<001>$ direction, Fig. 3.6. This suggests that the shear stresses $s_{yz} + s_{zx} + s_{xy}$ of Eq. 3.10 couple $F_0$ to $A$. The coupling cannot, in practice, be determined from the data in Fig. 3.4. However, the value of the shear parameter $A_2 = 3.7$ meV/GPa corresponds to a strain parameter of $c_{44}A_2 = 0.3$ eV/strain, again of a similar magnitude to $c_1'$.

### 3.7 Thermal quenching of the luminescence

We have examined the decay characteristics of the $A-B-C$ system. The measured decay times were found to be exponential over the entire temperature range and identical within the experimental error for all the components. This serves as an independent confirmation that the whole band corresponds to transitions at the same center. Figure 3.9 illustrates intensity decay of the lines $A$, $B$, and $C$ experimentally measured at 15 K. A lifetime of $\sim 150 \mu$s can be determined.

As one can see from Fig. 3.10, a strong variation of the decay times with temperature has been determined in the experiment. From a comparison with the
3.7. Thermal quenching of the luminescence

Figure 3.9: Decay time characteristics for the lines A, B, C of the 780-meV PL band measured at 15 K.

temperature dependence of the PL intensity, it seems natural to assume that the high-temperature decrease ($T \geq 30$ K) of the lifetime is due to the dissociation of the exciton. From the experiment we can conclude that the decay times of the A and B lines are identical. Also the decay time of line C, whose intensity allowed accurate measurements for $T \geq 10$ K, has a similar value. Such a situation is in agreement with the hypothesis that the A, B and C PL lines are due to transitions originating from three thermalizing states of the same center [25]. At low temperatures, we obtain long decay times of about 250 $\mu$s. This value is large when compared with the lifetimes of donor or acceptor bound excitons in silicon, which are in the nanosecond range. For excitons bound to a donor or to an acceptor, the lifetime strongly depends on the impurity binding energy $E_i$. Experimentally, approximate dependencies $\tau \propto E_i^{-4.6}$ for an acceptor or $\tau \propto E_i^{-3.9}$ for a donor were reported and the lifetime shortening was attributed to a localized phononless Auger recombination process [42, 43]. For example, for excitons localized at In acceptors in silicon with $E_i = 154$ meV, a lifetime of $\tau = 2.7$ ns has
been determined [44]. The lifetimes measured in this study are longer by factor of $10^5$. This indicates that nonradiative lifetime shortening processes are absent, or heavily suppressed, in this case. For silicon such a situation would occur for an exciton trapped at an isoelectronic center [45–48].

![Graph showing temperature dependence of luminescence intensity and decay times](image)

Figure 3.10: The intensity (arbitrary units) of the total luminescence from the band as a function of temperature is shown by the triangles. The temperature dependencies of the measured radiative decay times of lines A and B are shown by the squares and crosses, respectively. The lines are the least-squares fit of Eqs. 3.21 and 3.22.

Figure 3.10 shows, as functions of temperature, the luminescence intensity integrated across all the band (triangles) and the radiative decay times of lines A (squares) and B (crosses), measured in independent samples. As the temperature increases to $\sim 35$ K, the total intensity increases with the increasing population of state C, from which transitions are strongly allowed (Sec. 3.3). The decrease at high temperature occurs generally for luminescence centers in silicon, Sec. 3.1. We know from Sec. 3.3 that all the excited states of the center reach thermal equilibrium before the PL transition occurs and so the intensity is expected to follow

$$I(T) \approx \frac{I(0) \left[ 1 + \sum_i (\tau_F g_i / \tau g_F) \exp(-E_i/kT) \right]}{1 + \sum_i (g_i / g_F) \exp(-E_i/kT) + (g / g_F) T^{3/2} \exp(-E_a/kT)}.$$  (3.21)
3.7. Thermal quenching of the luminescence

Here the sums are over all the states \( i = A, B, \) and \( C \) and \( 1/\tau_i \) is the mean transition probability for the radiative transitions originating each of the \( g_i \) degenerate states of the state at an energy \( E_i \) above \( F_0 \). The thermal quenching of the excited states has an activation energy \( E_a \) and an effective degeneracy of \((g/g_F)T^{3/2}\) relative to state \( F_0 \).

The decay times as measured for lines \( A \) and \( B \) from 4 to 50 K are also shown in Fig. 3.10. Lines \( A, \) \( B, \) and \( C \) decay exponentially with time after a pulse of excitation. Since their excited states are in thermal equilibrium, Sec. 3.3, their decay times are equal at each temperature. Corresponding to Eq. 3.21, the decay time \( \tau \) is given by

\[
\frac{1}{\tau(T)} = \left( \frac{g_F}{\tau_F} \right) \left[ \frac{1 + \sum_i (\tau_F g_i/\tau_i g_F) \exp(-E_i/kT) + (r_g/g_F)T^{3/2} \exp(-E_a/kT)}{1 + \sum_i (g_i/\tau_i g_F) \exp(-E_i/kT) + (g/g_F)T^{3/2} \exp(-E_a/kT)} \right].
\]

(3.22)

Here the term \( r \) determines the rate of ionization into the continuum.

In Eqs. 3.21 and 3.22, the values of \( E_i \) are known from the optical spectra, and \( g_F = 6, \) \( g_A = 5, \) \( g_B = 3, \) and \( g_C = 1. \) from Secs. 3.5 and 3.6. From the measured ratio of the probabilities of transitions \( F, \) \( A, \) and \( B, \) Eq. 3.1, we know the ratios \( \tau_F/\tau_A \) and \( \tau_B/\tau_A: \tau_F/\tau_A = (I_A g_F/I_F g_A) = 1.8 \) and \( \tau_B/\tau_A = (I_A g_B/I_B g_A) = 0.9. \) The thermal-quenching energy \( E_a \) is best found from the luminescence data. It is not sensitive to the other parameters, and a least-squares fit gives \( E_a = 33.3 \pm 1 \) meV. This value is in agreement with the threshold of photo-ionization from the excited states \( (E_a=33 \) meV, Ref. [49]). It is also comparable to the value of 41.7 meV for the binding energy relative to state \( C, \) derived indirectly by assuming that the transition at 816 meV involves an effective mass electron in a \( 2p_0 \) state, which can be compared to the energy levels of a donor [28]. The value of \( E_a \) has been fixed at \( 33.3 \) meV. A least-squares fit of Eqs. 3.21 and 3.22 to all the data in Fig. 3.10 can now be made with five adjustable parameters. They are determined as \( \tau_A = 1020 \) \( \mu s, \) \( \tau_C = 6.3 \) \( \mu s, g = 490 \) \( K^{-3/2}, \) and \( r = 435, \) plus the physically insignificant \( I(0) = 60. \) Variations in the fitting strategy can change \( \tau_A \) and \( r \) by 50%, while \( \tau_C \) and \( g \) appear to be stable to \( \pm 10%. \) Radiative decay times in the microsecond range are typical for centers in silicon with diffuse excited states. From the parameters, we have \( I_F/I_C = (g_F \tau_C)/(g_C \tau_F) = 0.02 \pm 0.01, \) confirming the value in Eq. 3.1.

We can now clarify why in our fitting procedure we first obtained the quenching energy \( E \) from the luminescence intensity. If there was no quenching, the luminescence would increase and saturate as state \( C \) became populated. The quenching therefore has a major effect on the total luminescence. In contrast, it has a smaller absolute effect on the lifetime, which is already severely reduced by the relatively

\[\ldots\]
short lifetime of the excited state of line C. By combining the data, we can estimate the rate of thermal ionization, which does not appear to have been presented for any pseudodonor in silicon. In Eq. 3.22 the term \((r_g/\tau_F) T^{3/2} \exp(-E_a/kT)\) represents the thermally activated quenching of the luminescence, which consists of a Boltzmann term and the usual preexponential, which is temperature dependent. At 50 K, the prefactor has the value \(4 \times 10^{10}\) Hz, surprisingly slower than the frequency (\(\sim 10^{12}\) Hz) of the dominant 5.8-meV phonon.

### 3.8 Summary

We have reported the results of a detailed phenomenological study of the optical properties of a silver-related center in silicon. Perturbations of the optical transitions by uniaxial stresses and magnetic fields have been accurately described in terms of an effective-mass electron, orbiting the center in a triply degenerate orbital state in effectively \(T_d\) symmetry, and a tightly bound hole, which has its angular momentum quenched by the local trigonal field of the center (Sec. 3.5). These particles couple through their spin. At a slightly lower energy than these readily observed states, a state exists from which optical transitions are strongly forbidden, but which is phonon-coupled to the other electronic states. As a result, the vibronic sidebands observed at low temperature derive from the forbidden no-phonon line (Sec. 3.6). Using an effective mass for the vibrational mode derived from isotope data (Sec. 3.4), we have shown that the required magnitude of the electron-phonon coupling is of a reasonable magnitude. With this energy-level scheme, the total luminescence and the radiative decay time have been fitted over the temperature range 4 - 50 K, and it has been shown that the data can give an estimate of the time taken to thermally ionize an electron from an effective-mass state (Sec. 3.7). A highly detailed phenomenological understanding of the optical properties can therefore be achieved, even though the molecular structure of the core of the center has not been determined.