Photoluminescence, Photoluminescence Excitation and Optically Detected Magnetic Resonance Spectroscopies on Defects in Semiconductors

Ivan G. Ivanov

Department of Physics, Chemistry and Biology, Linköping University, 581 83 Linköping, Sweden

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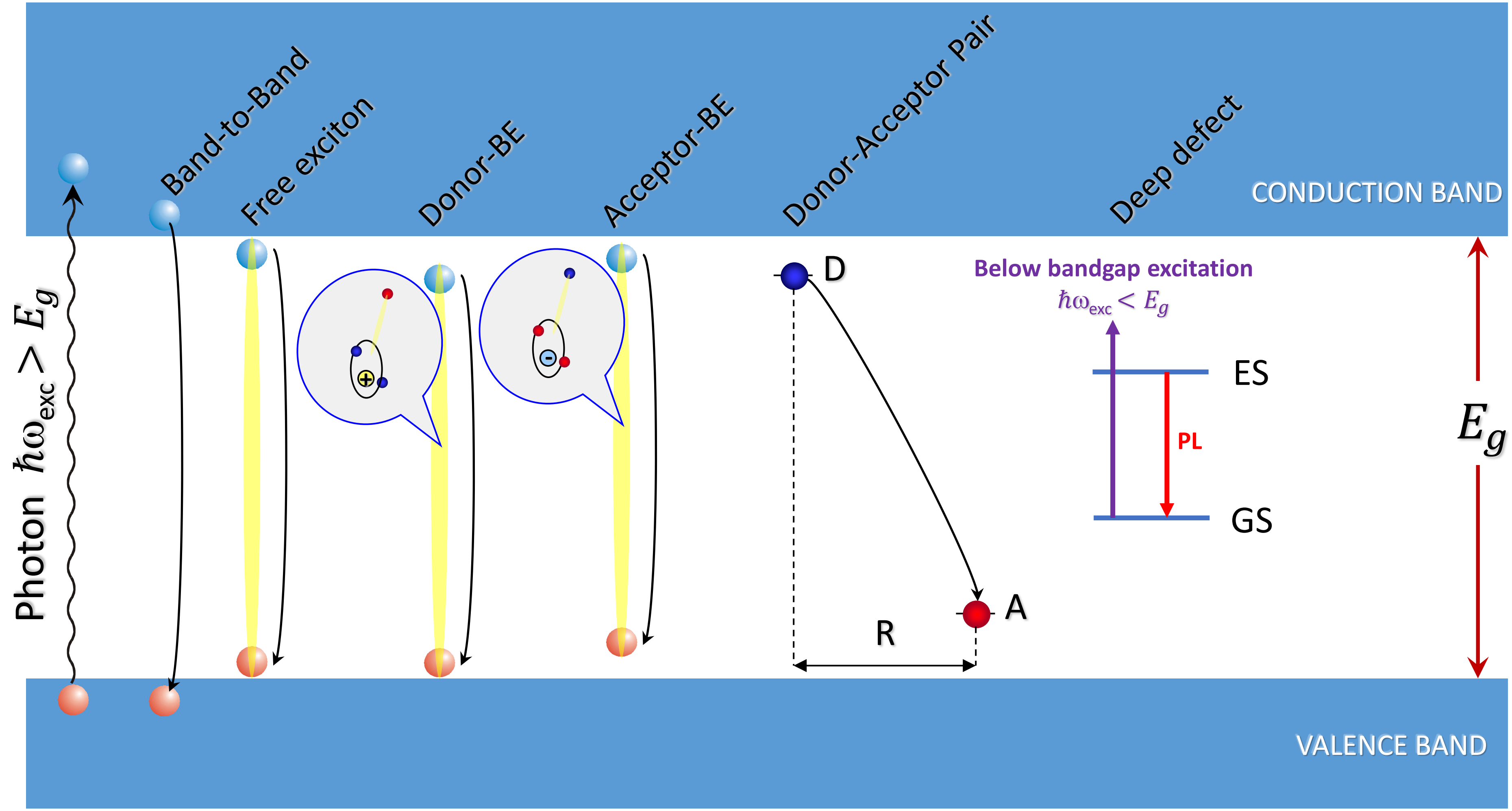
OUTLINE

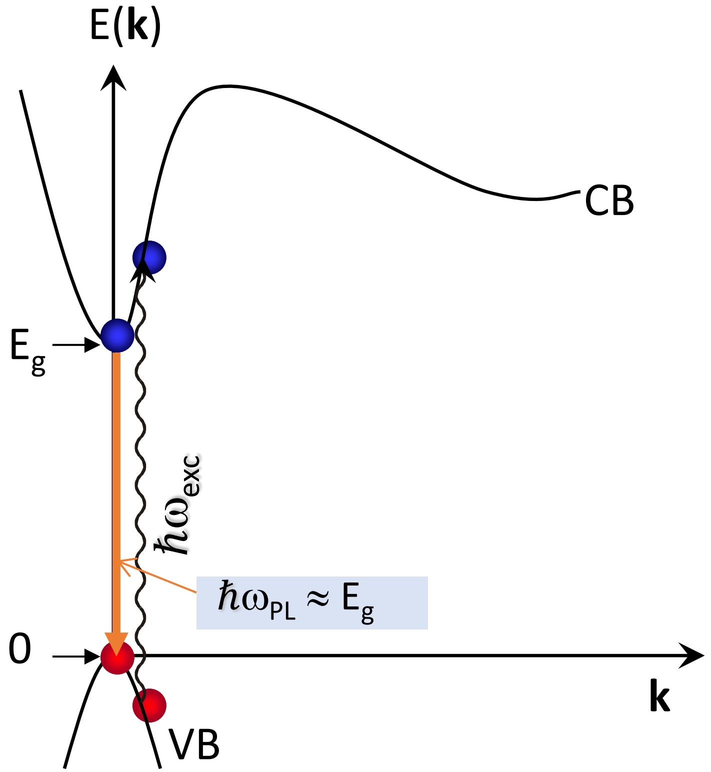
1. Types of photoluminescence (PL) in semiconductors.
2. Basic concepts: Excitons, shallow and deep defects, intrinsic and extrinsic defects, radiative and non-radiative recombination.
3. Photoluminescence from shallow and deep defects.
4. The Photoluminescence Excitation (PLE) and Optically Detected Magnetic Resonance (ODMR) techniques.
5. Examples of PL and ODMR spectra for some defects in SiC. Photoluminescence quenching and charge state stability.
6. Single defects: creation, instrumentation and methods for their detection.
7. Polarization selection rules

Excitation and recombination



Excitation and recombination: Direct and indirect bandgaps

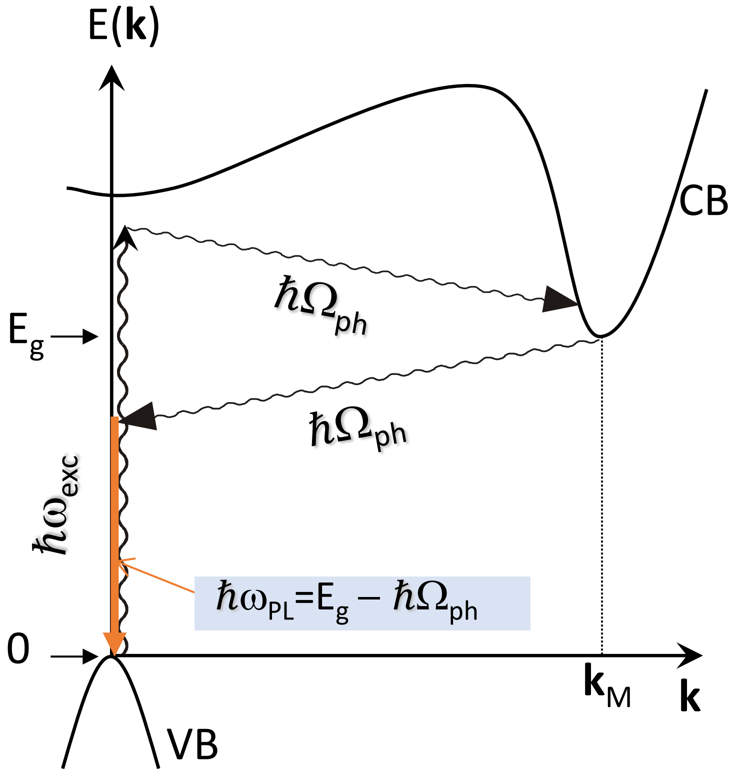
Direct bandgap



Energy conservation: $\hbar\omega_{exc}=E_e+E_h > E_g$

Momentum conservation: $\mathbf{k}_{exc}=\mathbf{k}_e+\mathbf{k}_h \approx 0$

Indirect bandgap



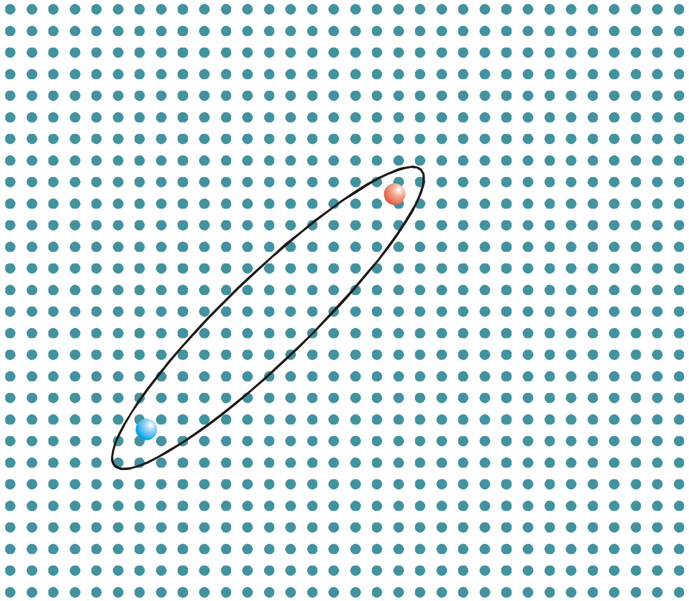
Energy conservation: $\hbar\omega_{exc}- \hbar\Omega_{ph}= E_e + E_h > E_g$, or $\hbar\omega_{exc} > E_g + \hbar\Omega_{ph}$

Momentum conservation: $\mathbf{k}_{exc}= \mathbf{k}_{ph} - \mathbf{k}_e + \mathbf{k}_h \approx 0$

$\rightarrow \mathbf{k}_e = \mathbf{k}_{ph}$

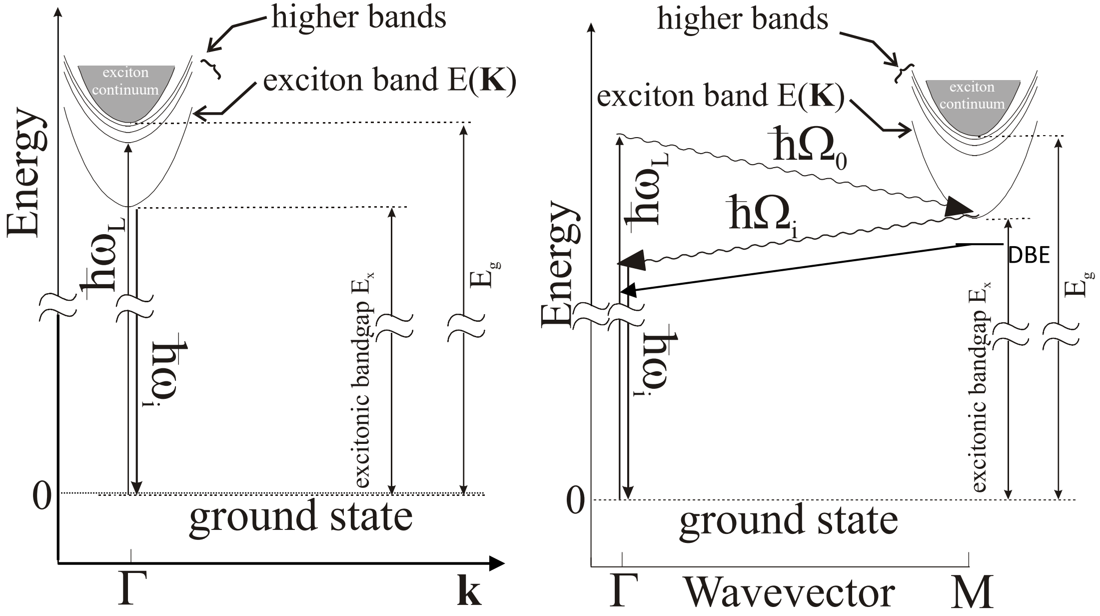
Basic concepts

Exciton



Excitonic and electronic bandgap

Direct bandgap / Indirect bandgap



Similar to the H-atom, except

- the masses of the two particles are similar;
- the Coulomb potential is expressed by $e^2/\varepsilon R$, instead of e^2/R

➢ a series of excited states are expected, similar to the H-atom:

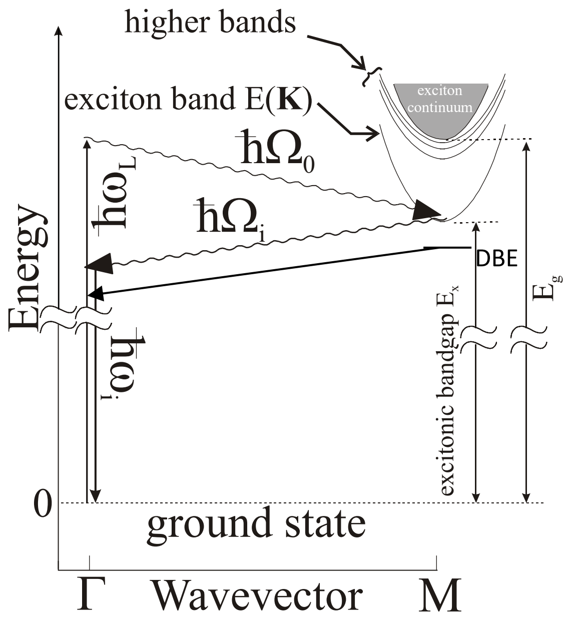
$$E_n = -E_0/n^2, \quad n = 1, 2, 3, \ldots$$

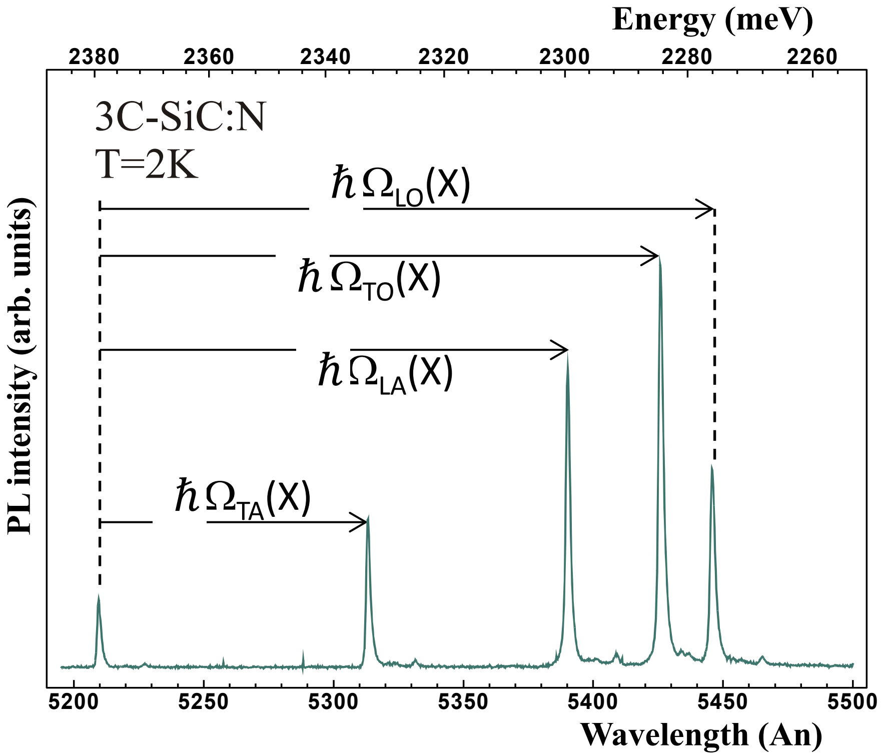
➢ the kinetic energy of the translational motion has to be accounted for:

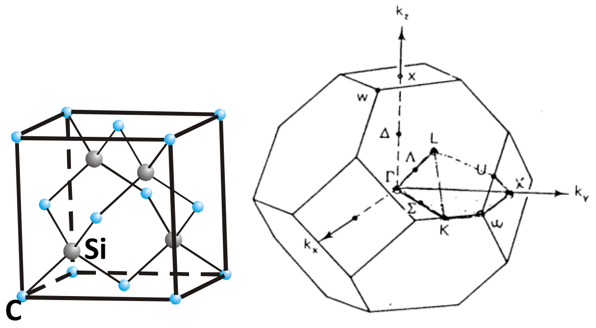
$$E_{total} = -E_0/n^2 + h^2k^2/2(m_e+m_h)$$

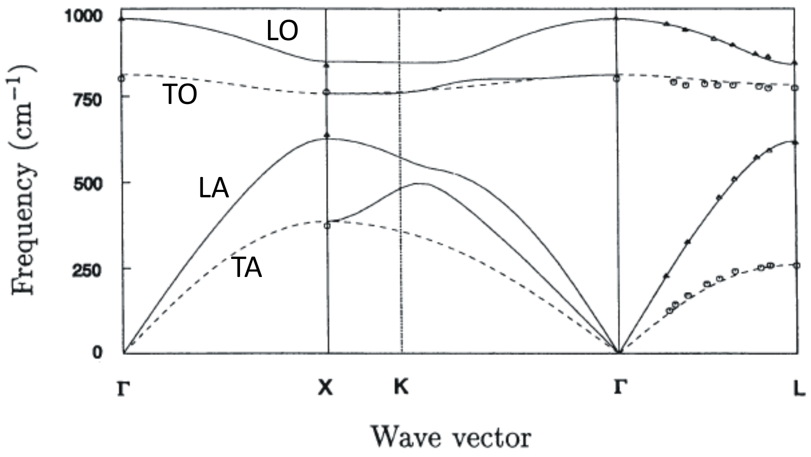
Indirect bandgap

PL spectrum of cubic SiC

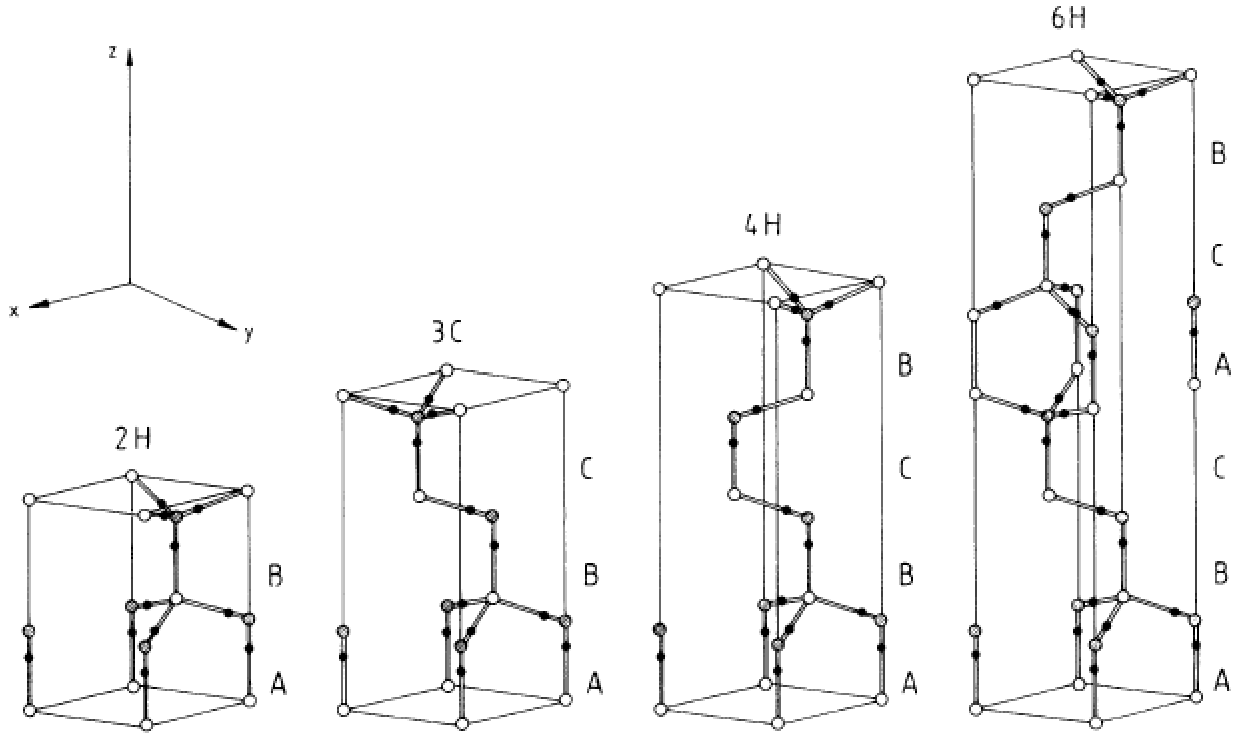


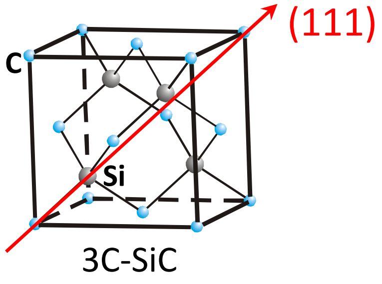


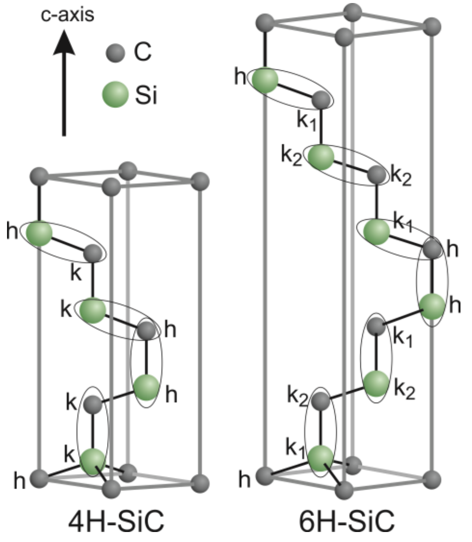




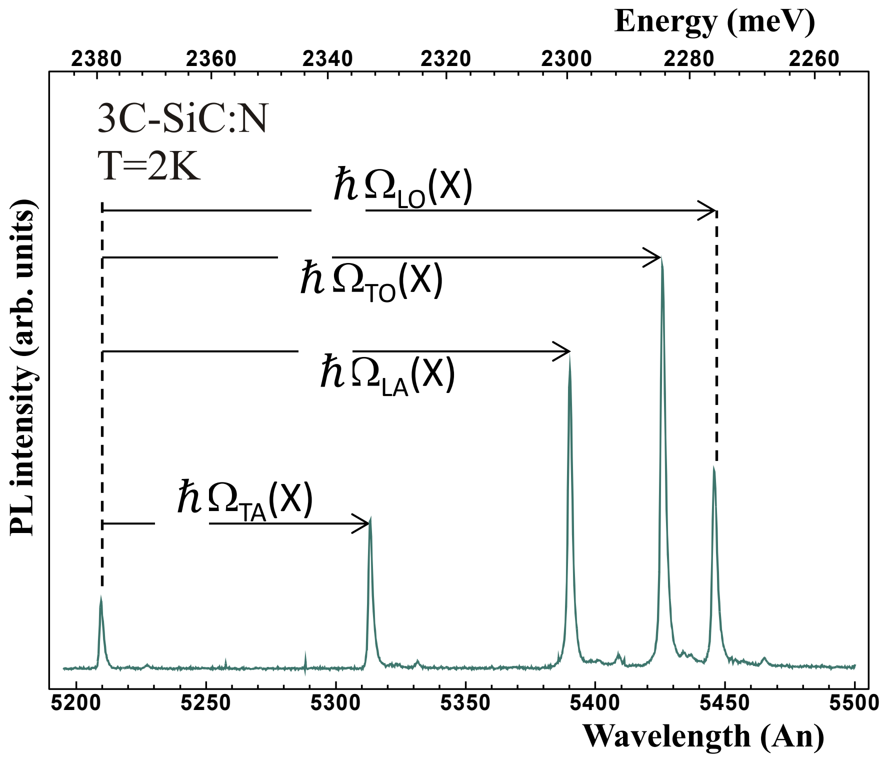
Polytypism in silicon carbide

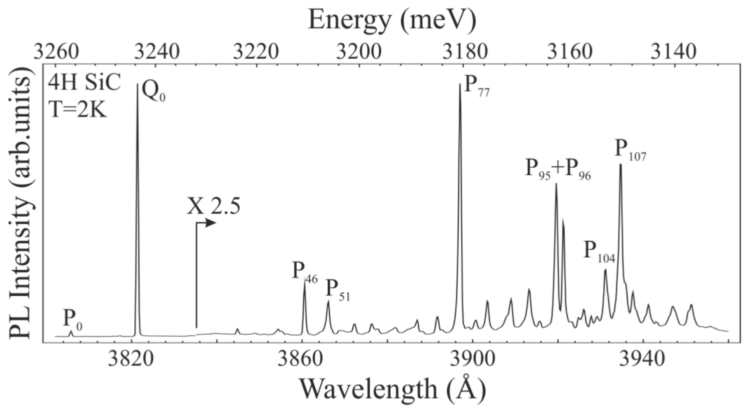


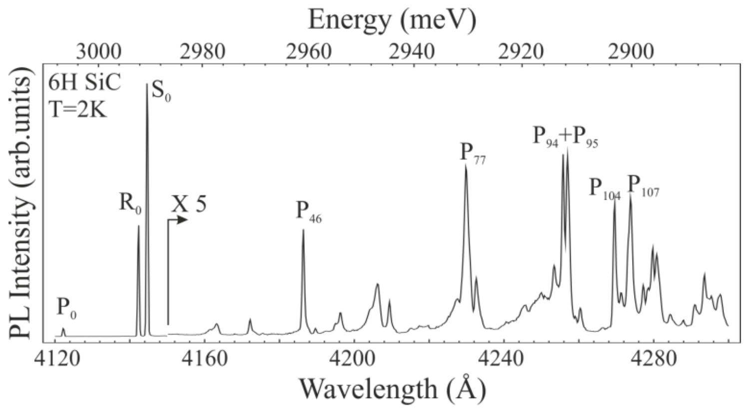




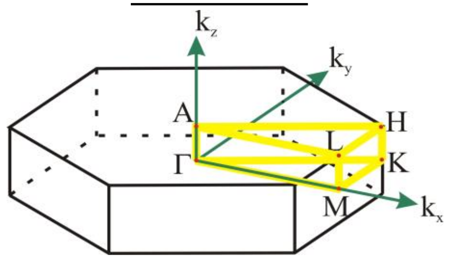
Inequivalent lattice sites . Bound exciton emission (N-BE)



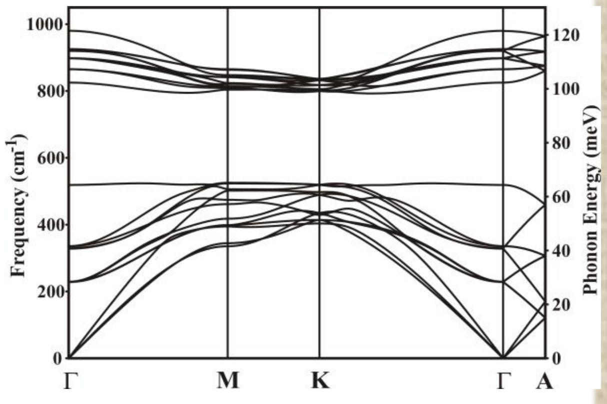




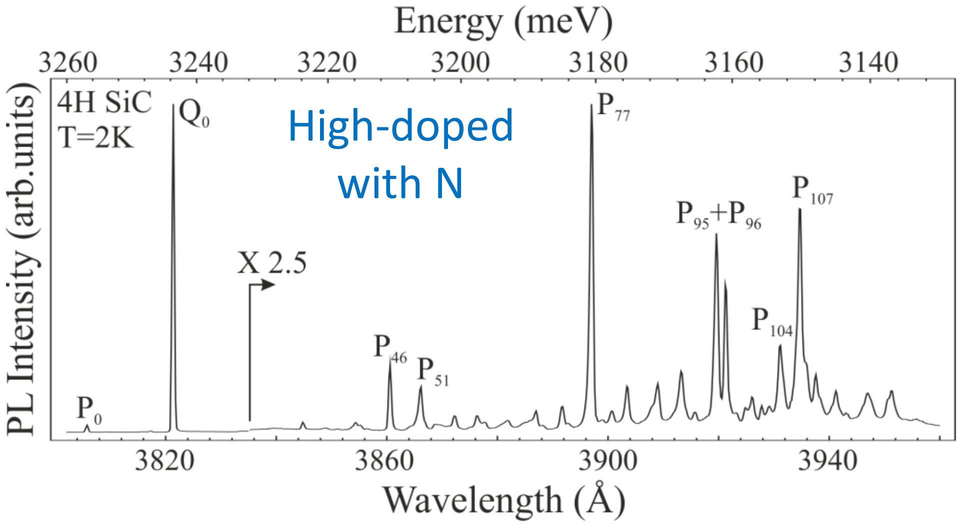
Brillouin zone

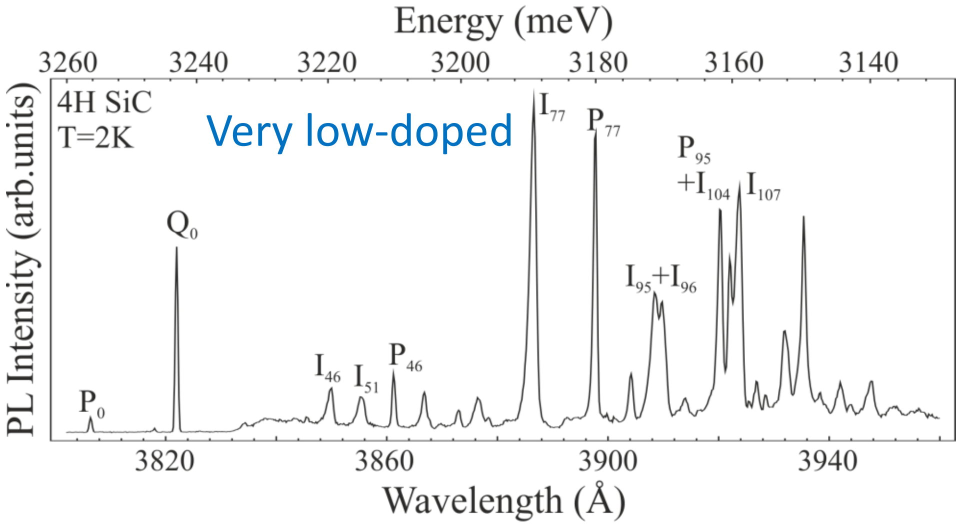


Phonon dispersion in 4H-SiC

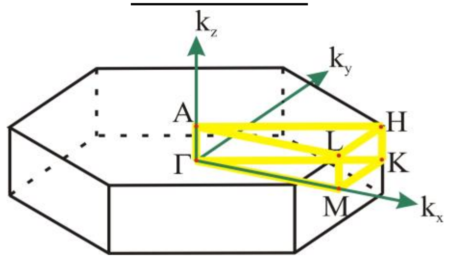


Inequivalent lattice sites. Free exciton emission

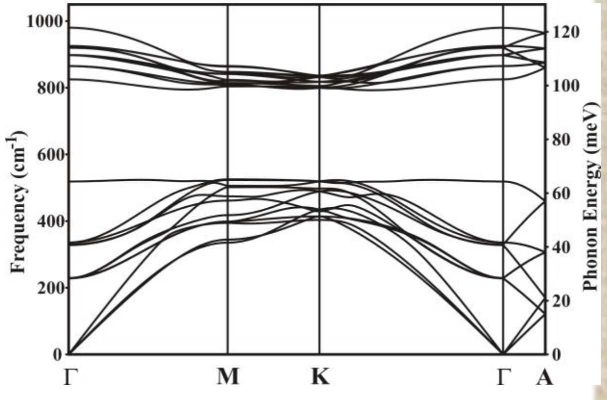




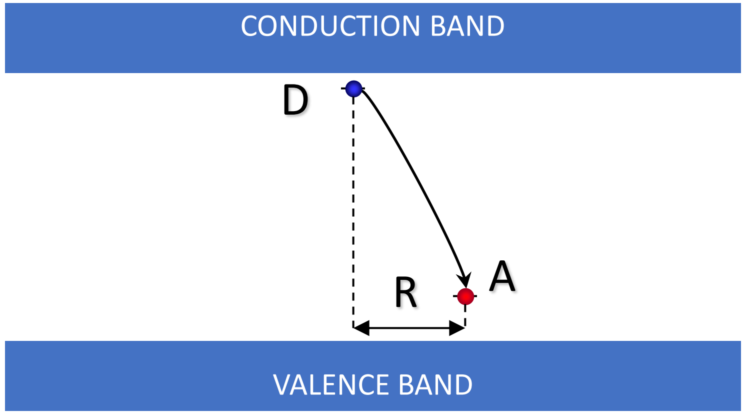
Brillouin zone



Phonon dispersion in 4H-SiC



Donor-acceptor pair luminescence

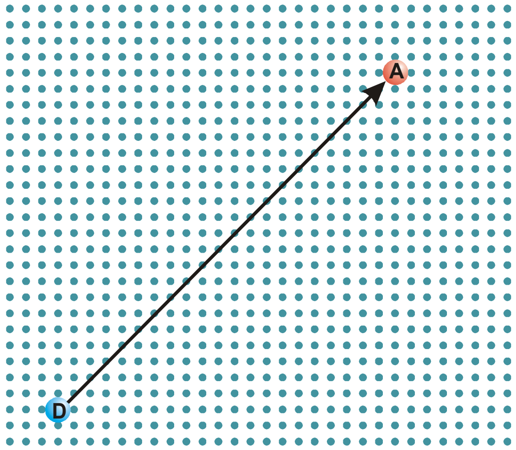


$\hbar\,\omega_{PL} = E_g - E_D - E_A + e^2/\varepsilon R + J(R)$

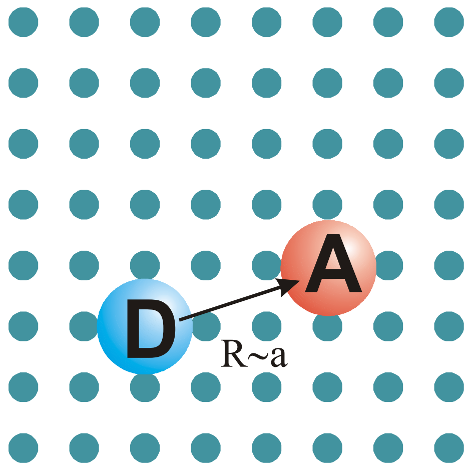
$J(R) \rightarrow 0$ when $R \rightarrow \infty$

$\rightarrow$ Model the DAP spectrum with J(R) = 0

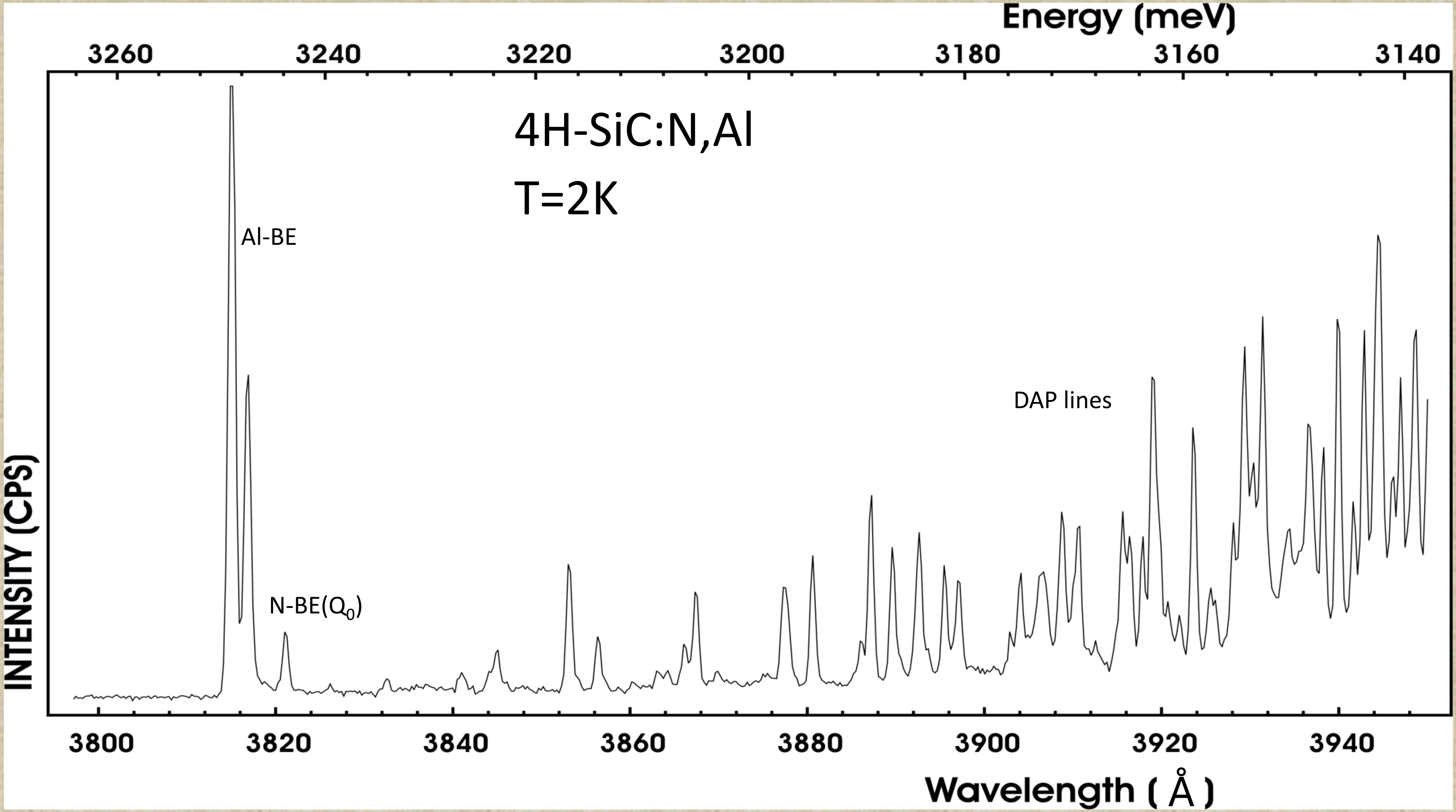
Remote pairs



Close pairs



Donor-acceptor pair luminescence



Photoluminescence from deep-level point defects

Characteristic features of deep-level defects

- “Deep level” means that the ground state (GS) is well separated in energy from the band edges.
- The excited state (ES) also is in the bandgap well separated from the band edges $\rightarrow$ wide bandgap semiconductors.
- The transition between the GS and the ES can be radiative or non-radiative. In many defects this transition can be considered as internal between two states (ES and GS) of the defect instead of recombination of an exciton bound to the defect.
- “Internal-to-the-defect” states means they are associated with the electronic structure of the defect. For impurity atoms, these states are often atomic levels split by the crystal field.
- Defects with spin and optical transitions are of interest for the quantum electronics (quantum technology).
- Each point defects has its own physics (in terms of mechanisms for excitation/recombination).

We shall consider some examples

Properties of the NV^- center and the divacancy in 4H-SiC: Electronic structure
(for the axial configurations, analogical to the electronic structure of NV^- centre in diamond)

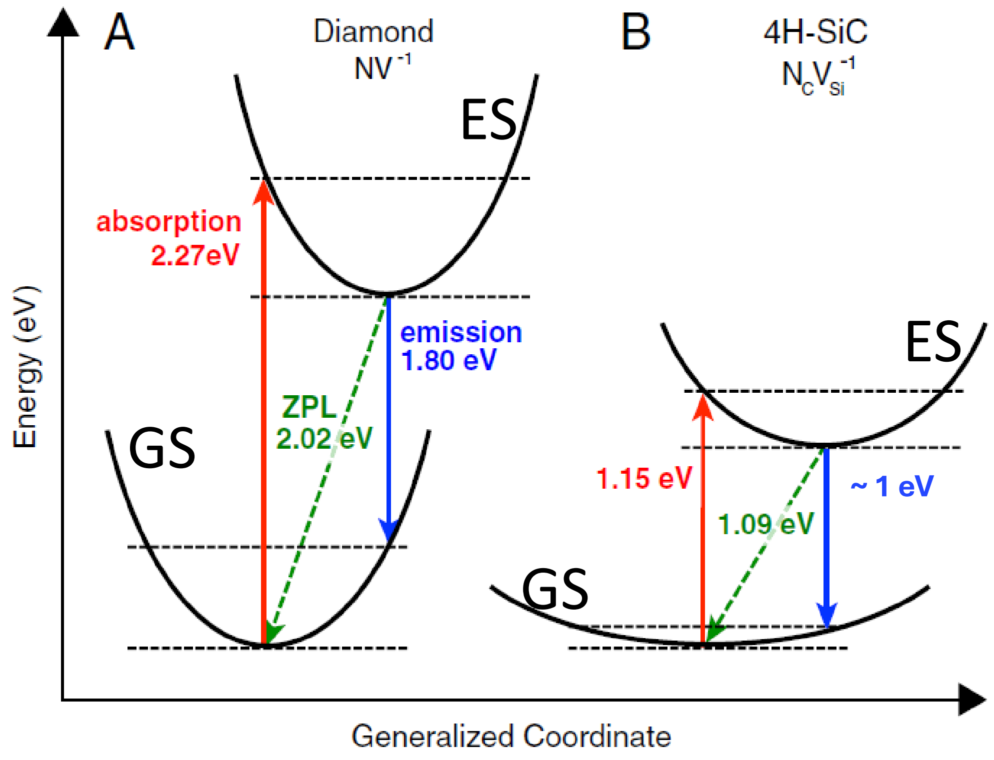
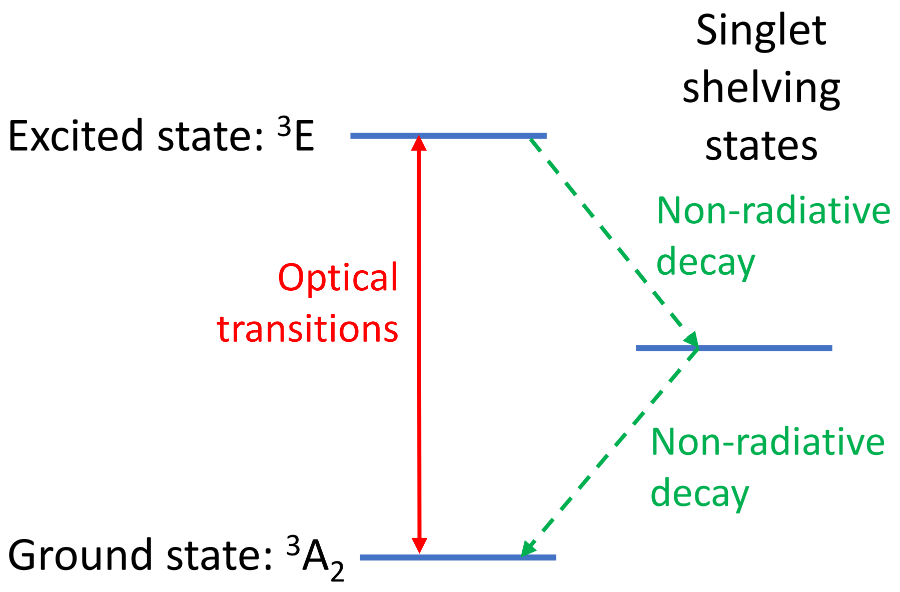


Fig. 4. Configuration-coordinate diagrams for spin-conserving triplet excitation. Excitation cycles for (*A*) the NV^{-1} center in diamond and (*B*) the $N_cV_{Si}^{-1}$ center in SiC are shown. Absorption, emission, and ZPL transitions are indicated, along with their energies.

The NV^- center and the neutral divacancy have spin $S = 1$

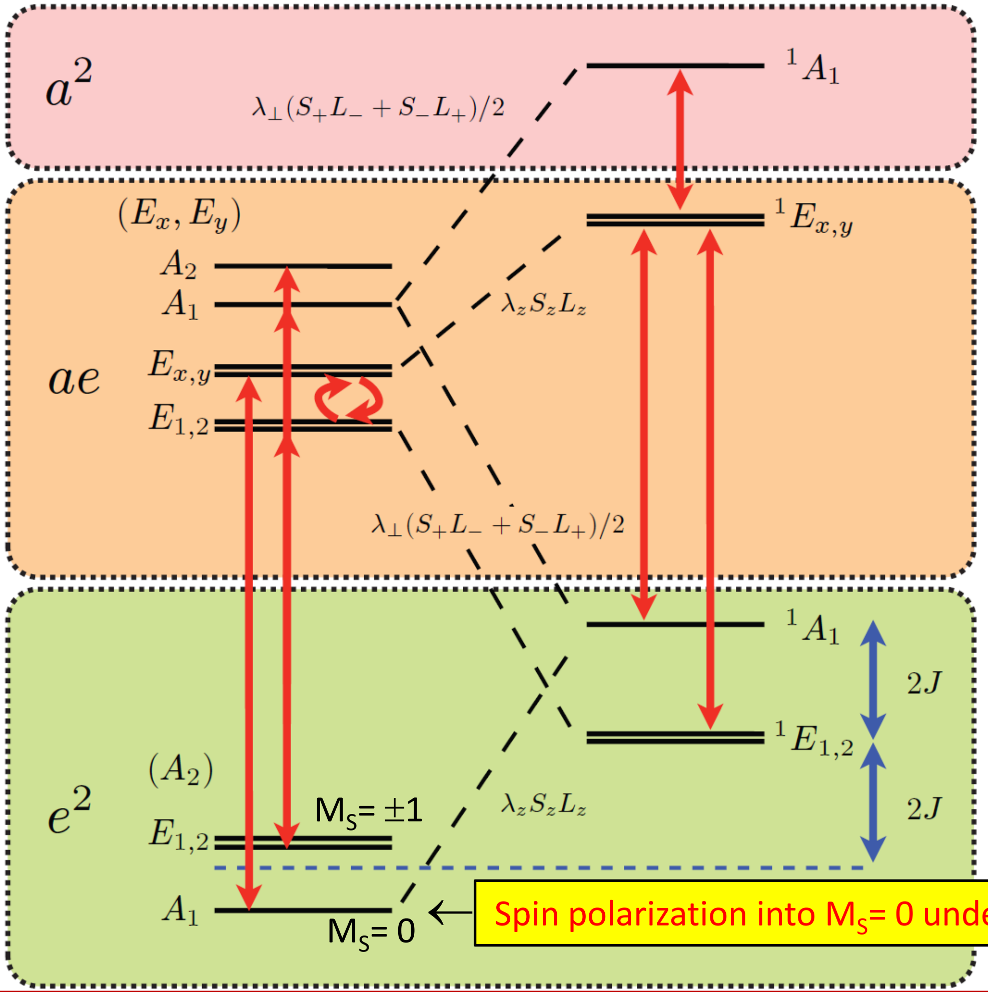


J.R. Weber *et al.*, PNAS | May 11, 2010 | vol. 107 | no. 19 | 8513–8518.

Properties of the divacancy in 4H-SiC: Electronic structure
(for the axial configurations, analogical to the electronic structure of NV^- centre in diamond)

Excited state: ^3E

Ground state: $^3A_2$



Singlet shelving states

Spin polarization into M_S= 0 under optical excitation

J.R. Maze, A. Gali *et al.*, New J. Phys. **13**, 025025 (2011) (diamond).
G. Bian, G. Thiering, A. Gali, "Theory of optical spin polarization of VV and NV in 4H-SiC", arXiv:2409.10233v1 (2024).

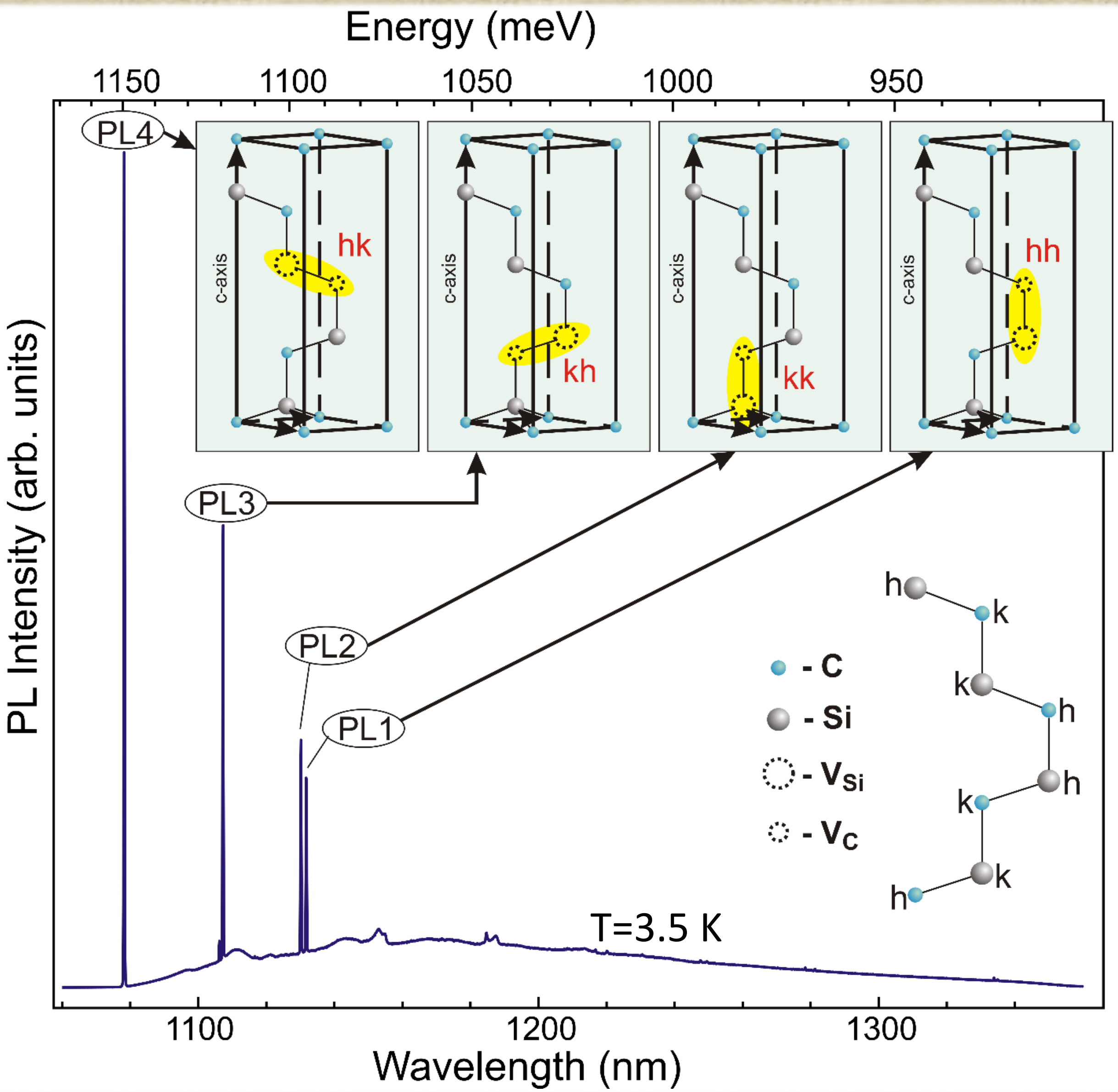
Example: The divacancy in 4H-SiC

EPR identification:
Son et al., Phys. Rev. Lett. **96**, 055501 (2006)

Gali et al., Mater. Sci. Forum **645-648**, 395 (2010)

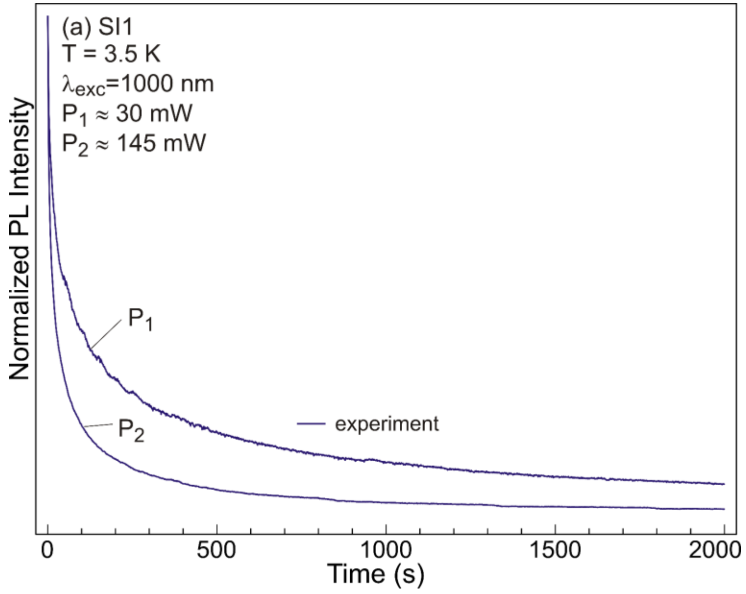
Baranov et al., Phys. Rev. B **83**, 125203 (2011)

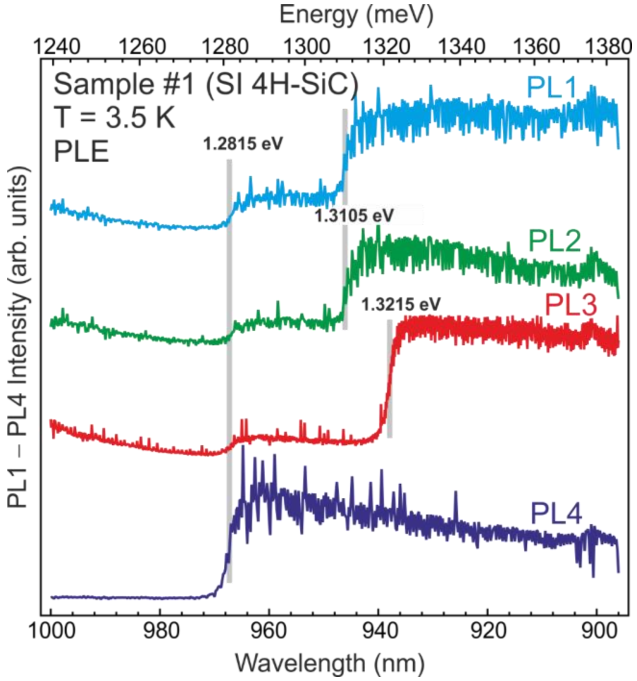
Christle et al., Nat. Mat. **14**, 160 (2015)

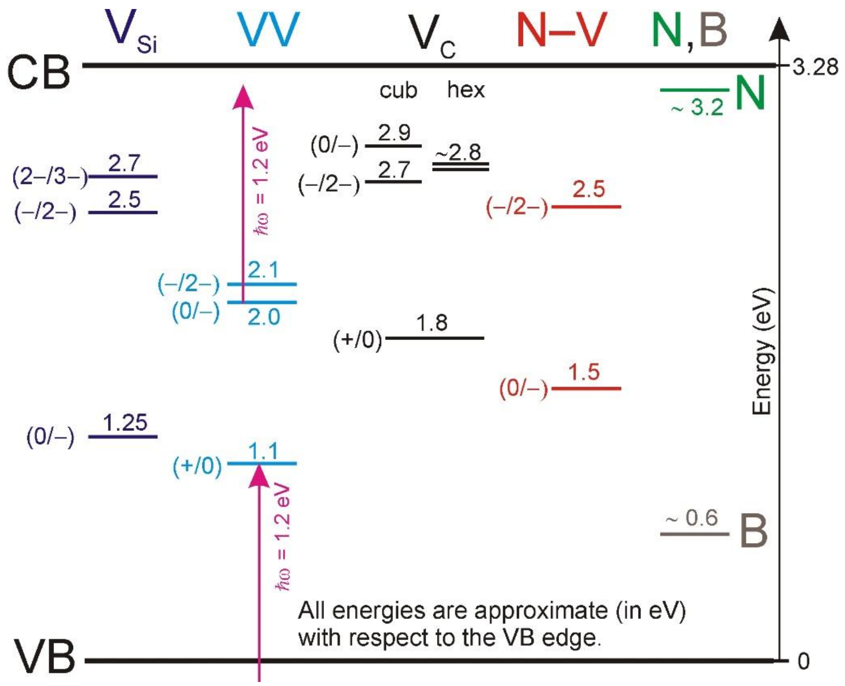


PL identification:
Koehl et al., Nature **479**, 84 (2011)

PL quenching





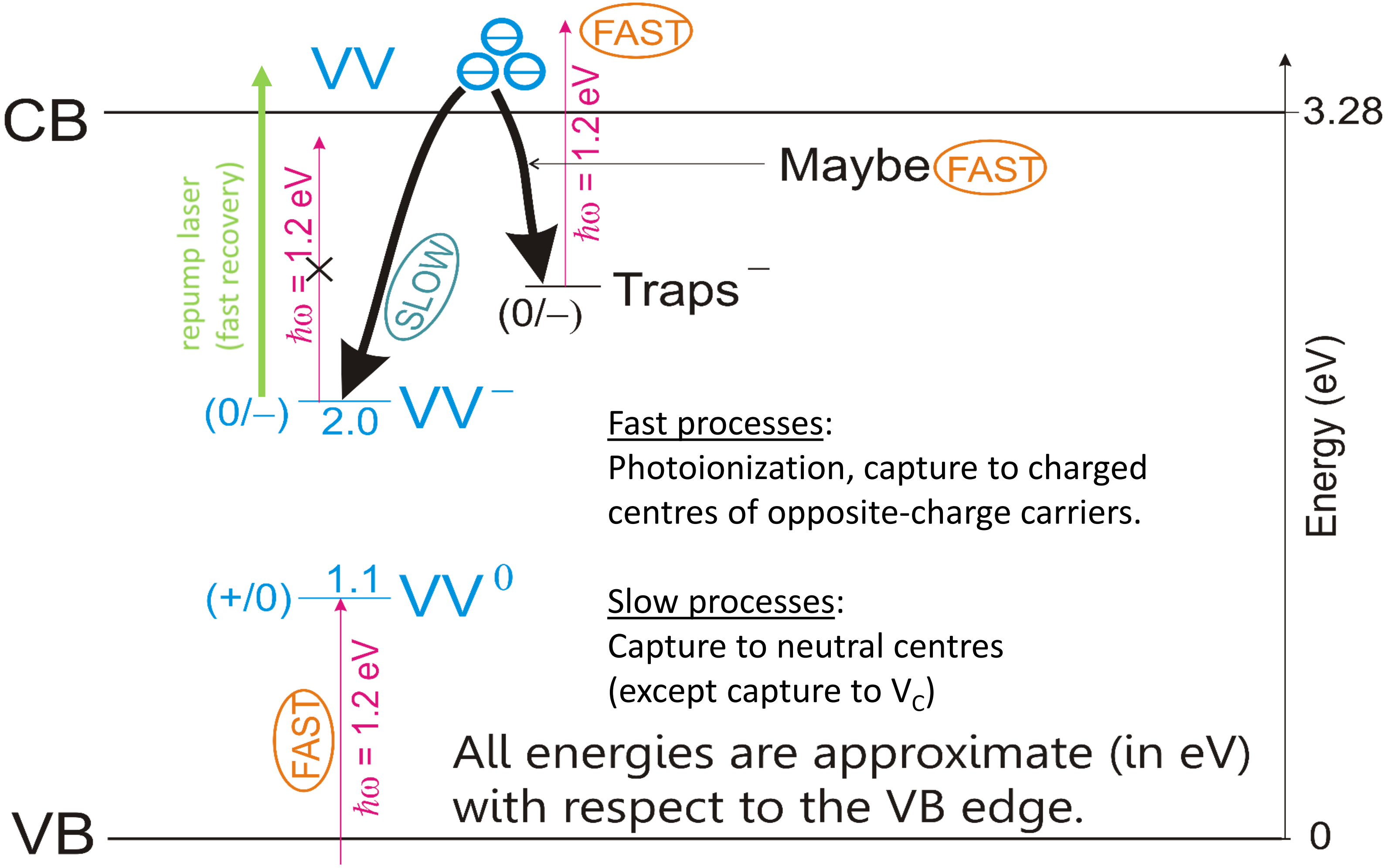


PL Line	PL1-PL2	PL3	PL4
Threshold energy (eV): Experimental Theoretical	 1.3105 1.245,1.209	 1.3215 1.307	 1.2815 1.174

Quenching mechanism

Model: Capture of electrons emitted from other traps

B. Magnusson et al., Phys. Rev. B 98, 195202 (2018)

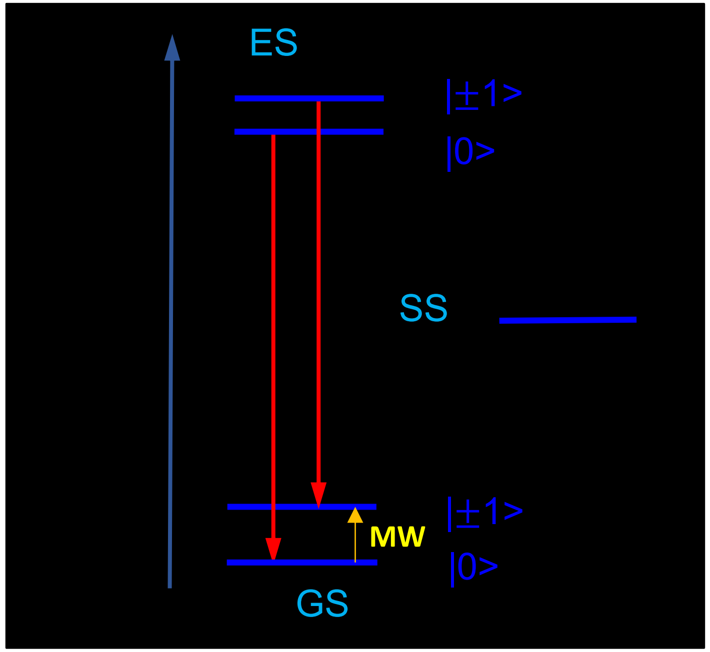


Fast processes:
Photoionization, capture to charged centres of opposite-charge carriers.

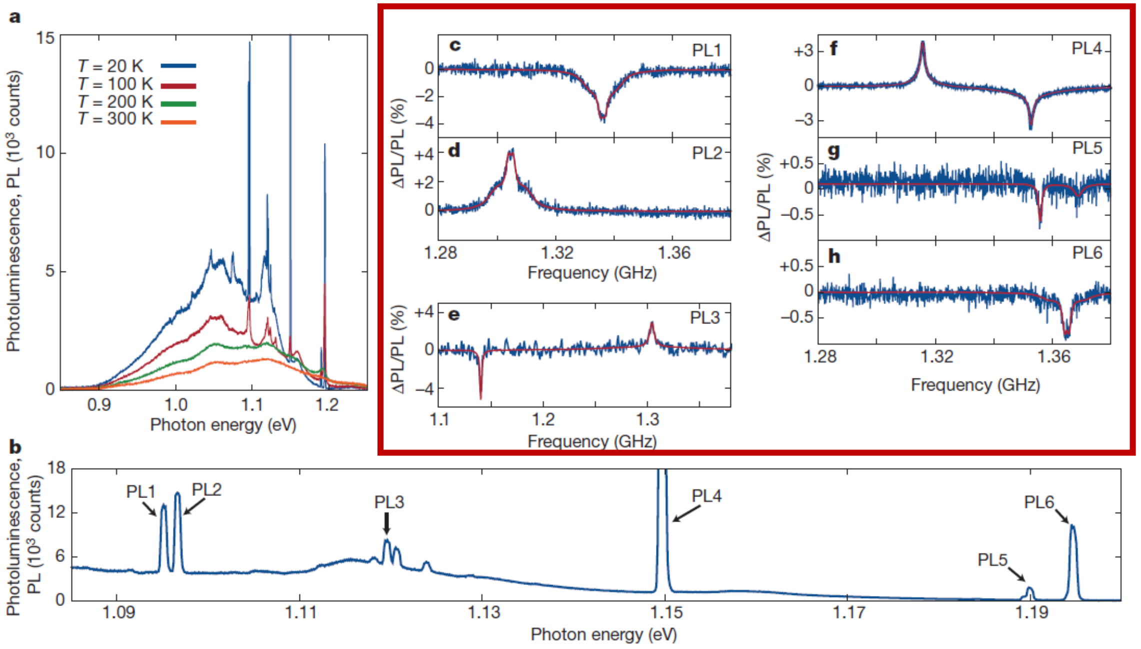
Slow processes:
Capture to neutral centres (except capture to V_C)

All energies are approximate (in eV) with respect to the VB edge.

The ODMR principle (Optically Detected Magnetic Resonance)



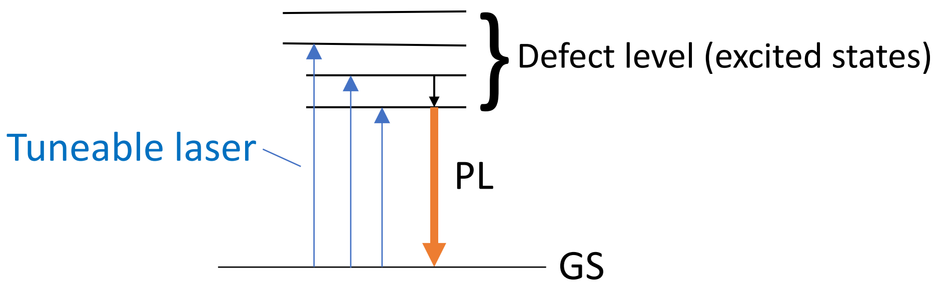
ODMR of PL1 – PL6



From: Koehl *et al.*, Nature **479**, 84 (2011).

ODMR: - the one transition is "brighter" than the other; hence dip (or peak) when the MW pulse is resonant with the energy between the spin sublevels of the GS.

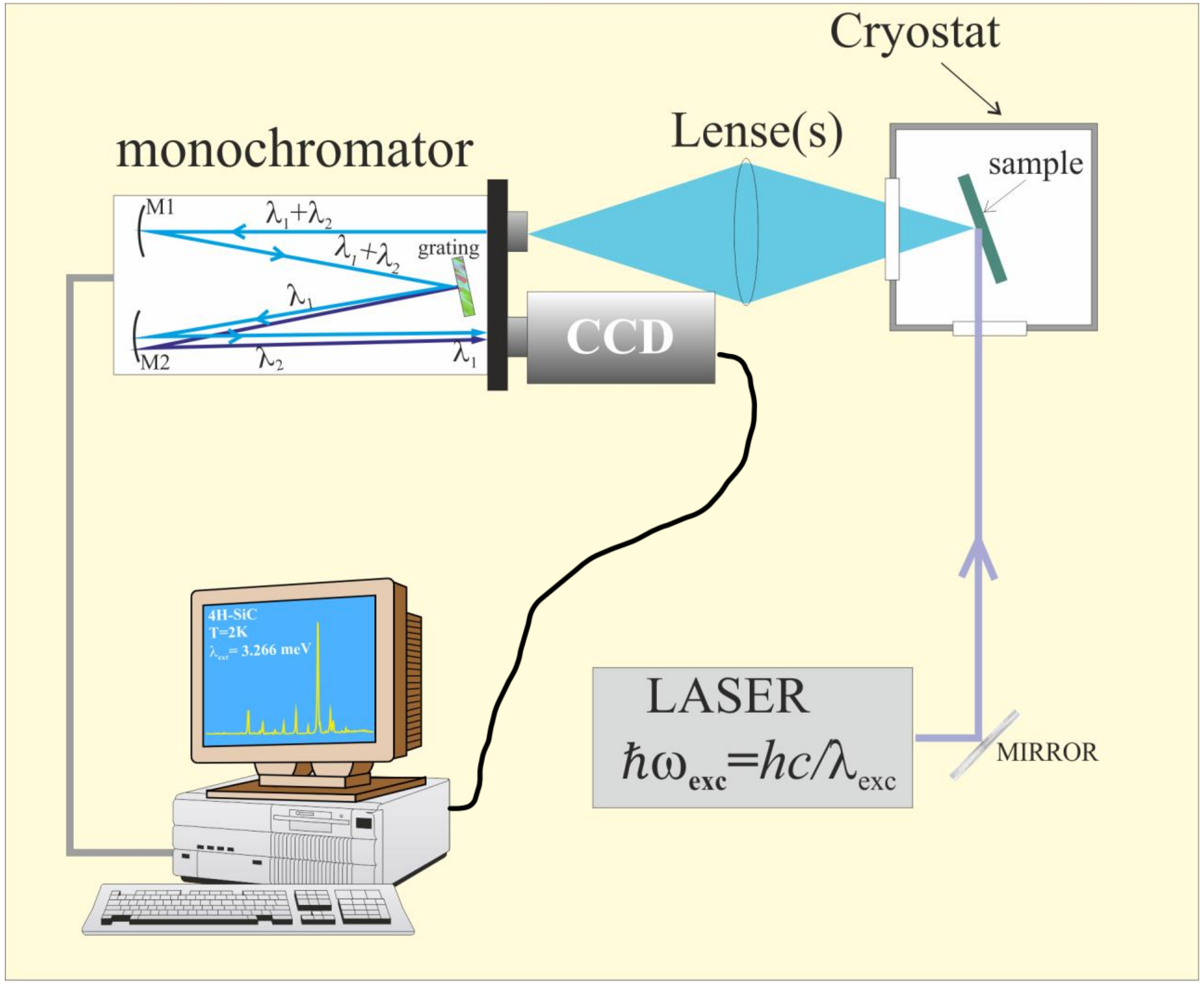
Basics of the photoluminescence excitation spectroscopy (PLE)



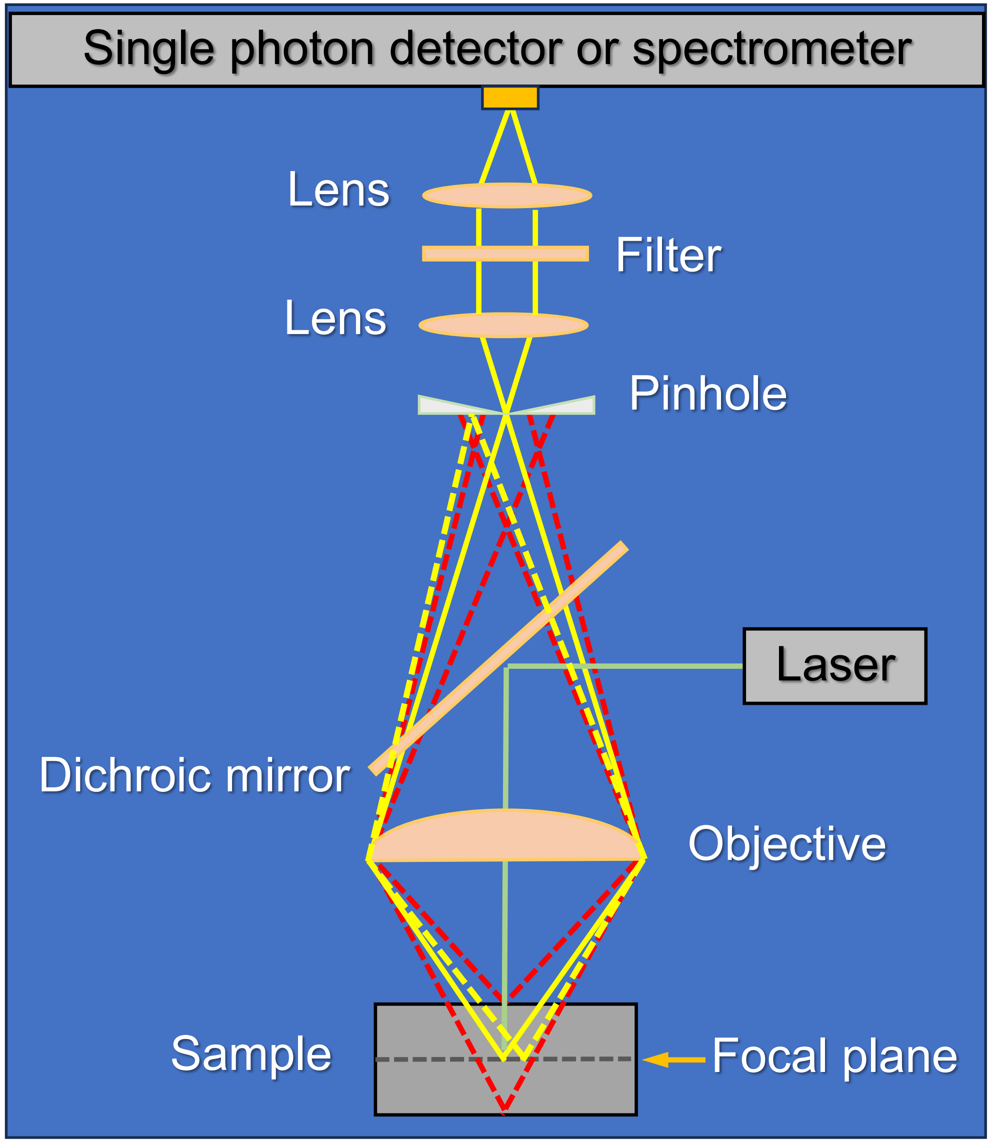
Benefits:

- Helps in investigating excited states at low T
- Helps to ”sort out” excited states belonging to different defects

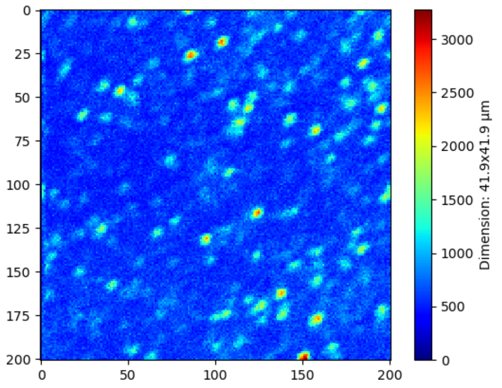
PL and PLE setup



Confocal microscopy for single defect studies

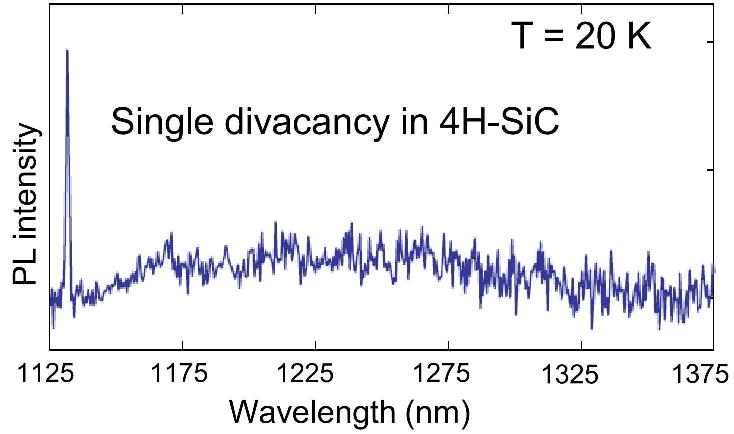


Single divacancy $V_C V_{Si}^0$ emitters in 4H-SiC

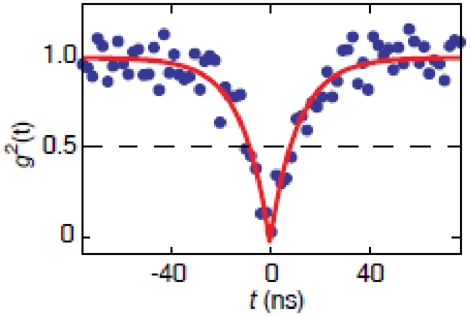


Single V_{Si}^- emitters in 4H-SiC

Confocal PL scan



PL spectrum of a single $V_C V_{Si}^0$ emitter



Photon antibunching

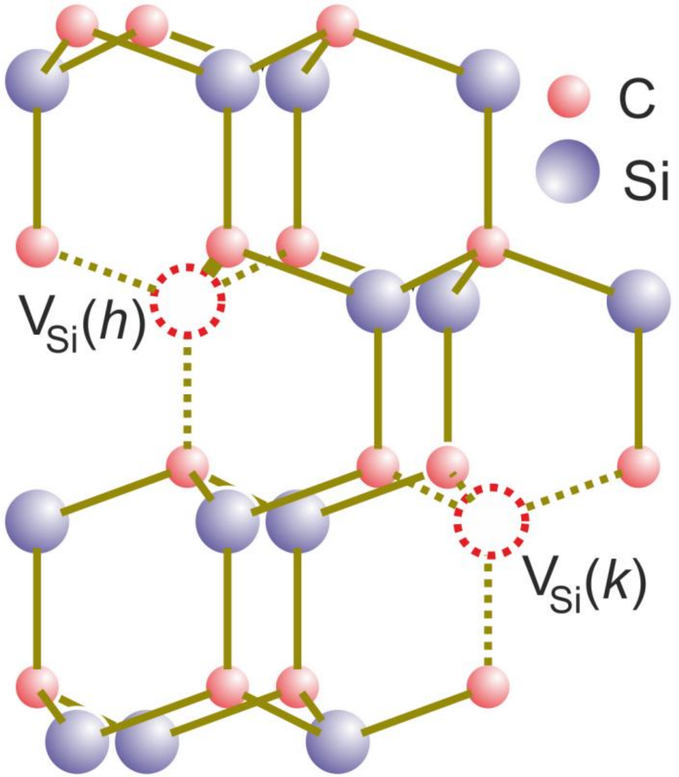
(Hanbury Brown and Twiss interferometer)

Photon antibunching (with the second-order correlation function $g^2(t=0) < 0.5$ is an indication of a single emitter

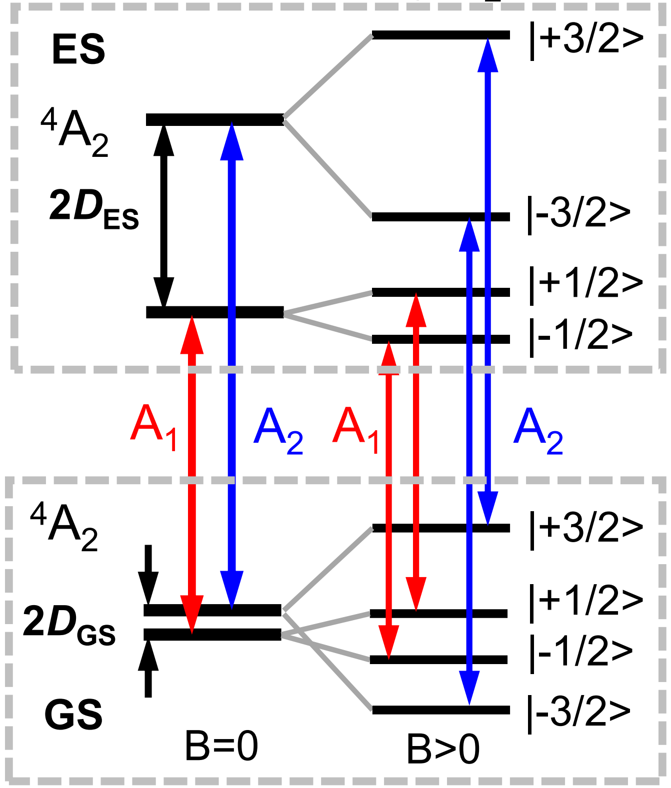
D.J. Christle et al., Nat. Mater. 14, 160 (2015)

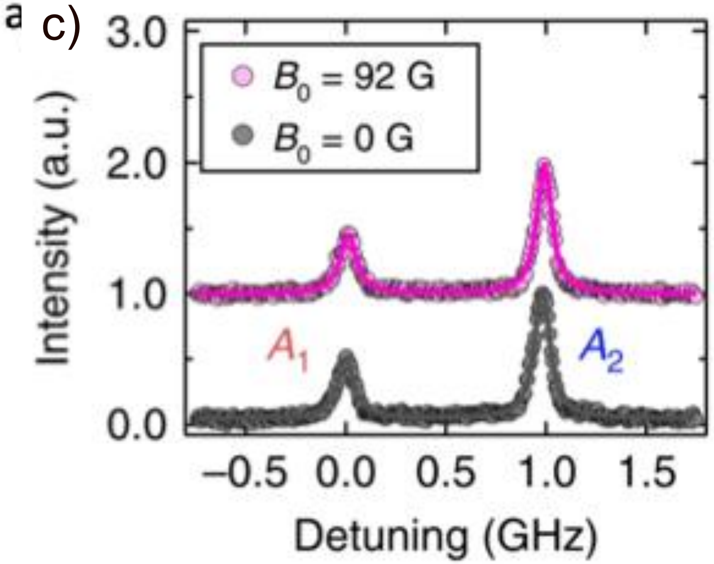
Example 2: Si vacancies in 4H-SiC

Spin qubit investigated

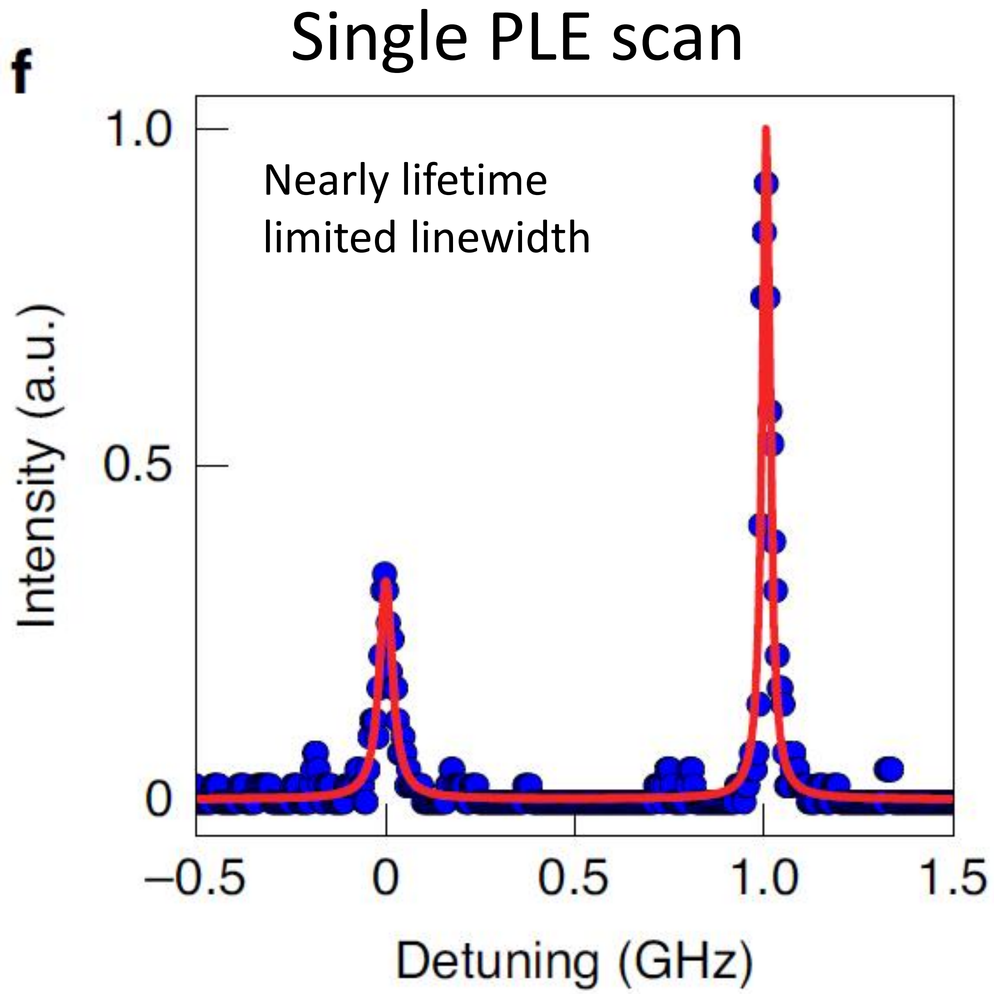


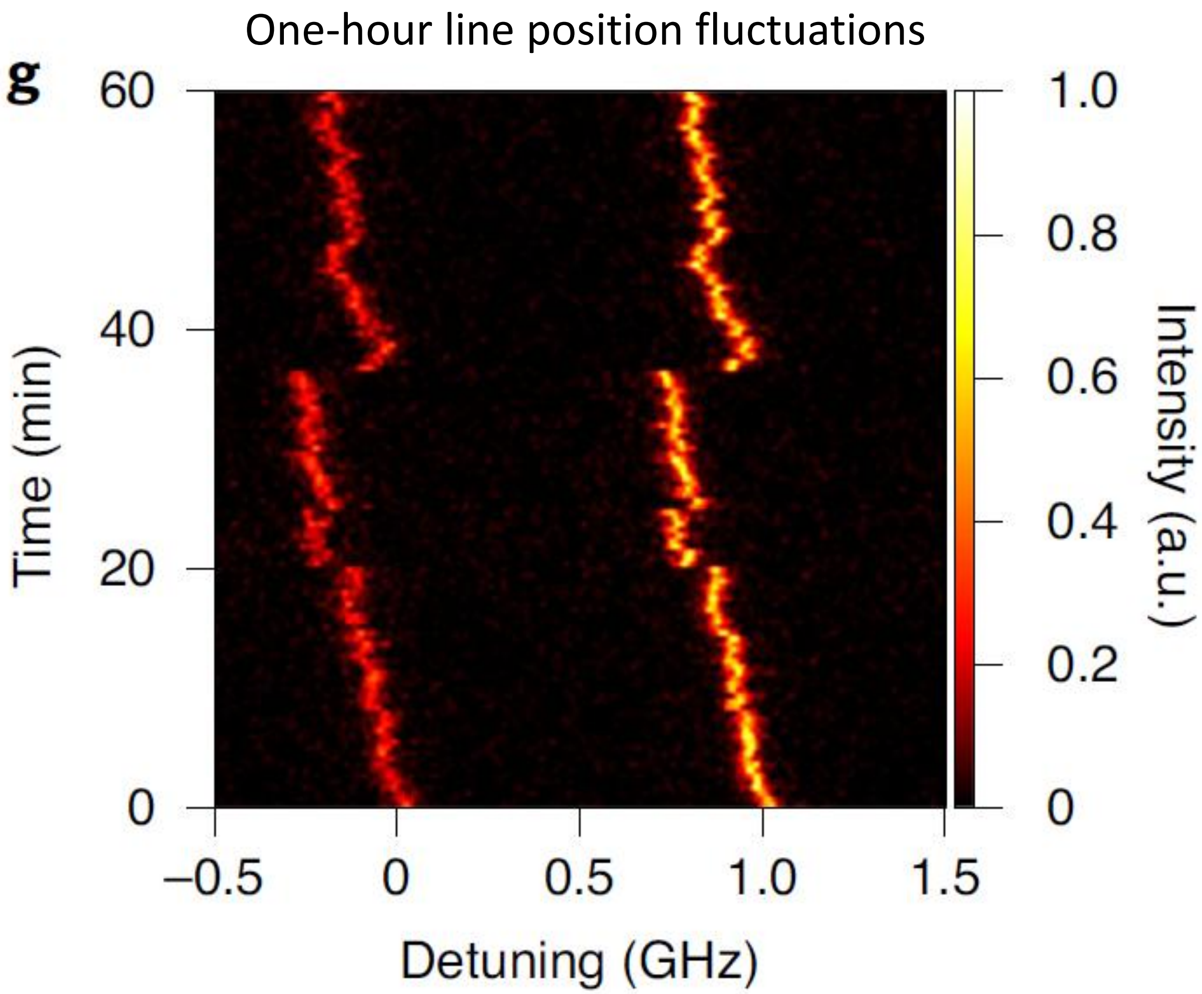
Si vacancy V_2





Spectral diffusion: Variations of the ZPL position due to interaction with environment

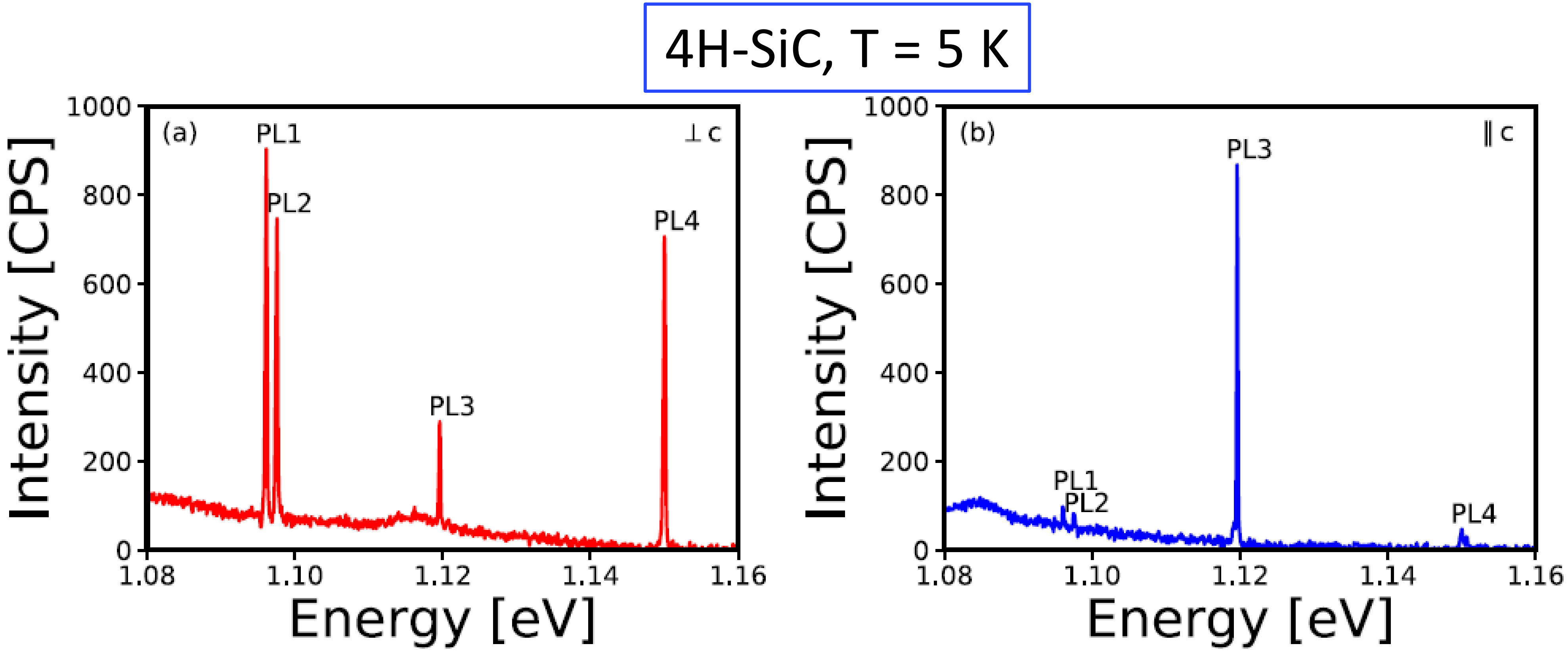




Babin *et al.*, Nat. Mater. **21**, 67 (2022).

Selection rules in PL, PLE, and in the excitation

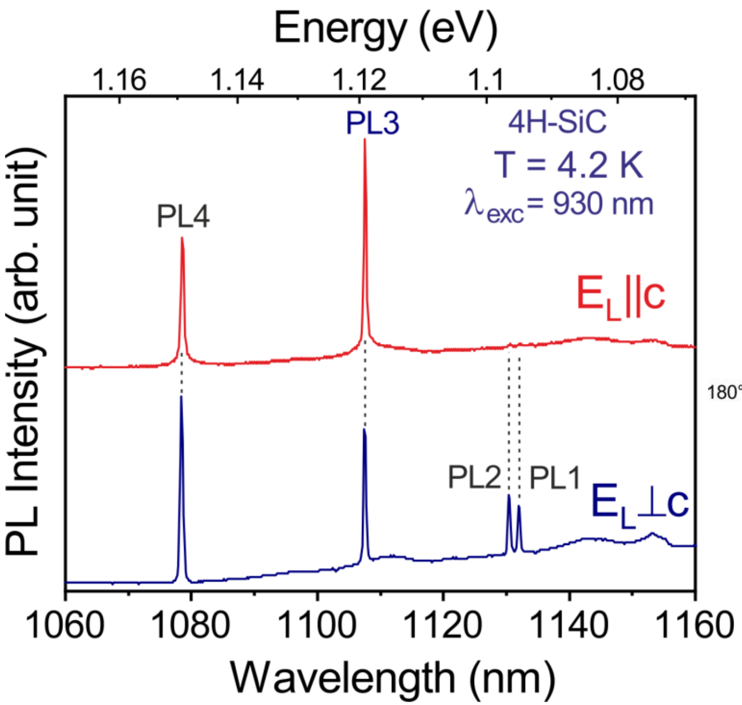
The divacancy lines have certain polarizations with respect to the crystal axis (e.g., in 4H-SiC)

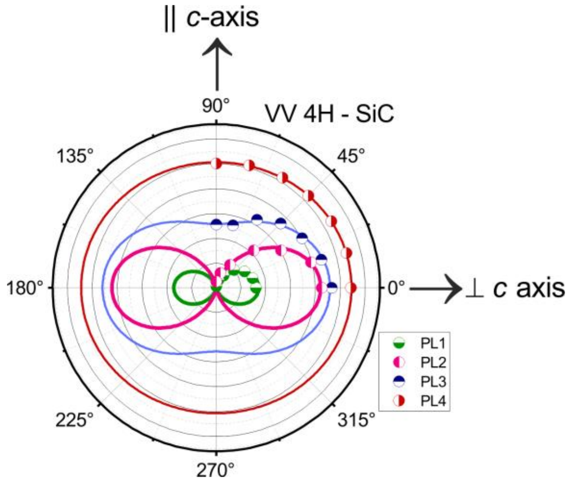


Properties of the divacancy in 4H-SiC: Excitation selection rules

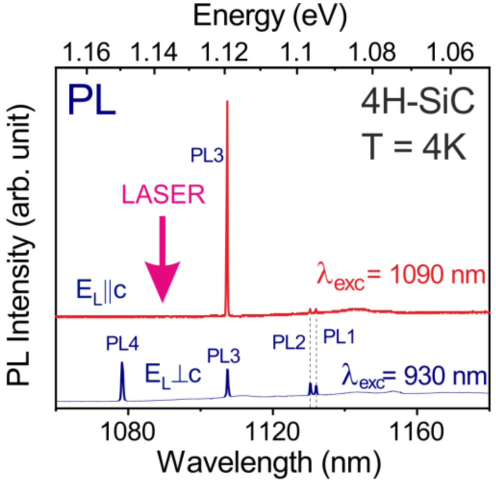
D. Shafizadeh, …, I.G. Ivanov, Phys. Rev. B **109**, 235203 (2024).

→ Selective excitation of PL3 alone is possible with laser with $E_L||c$ polarization and energy between PL3 and PL4.

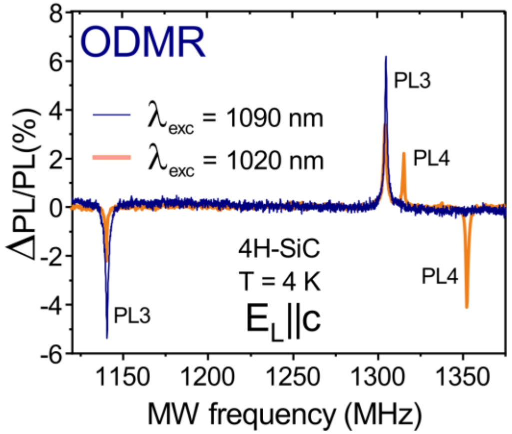




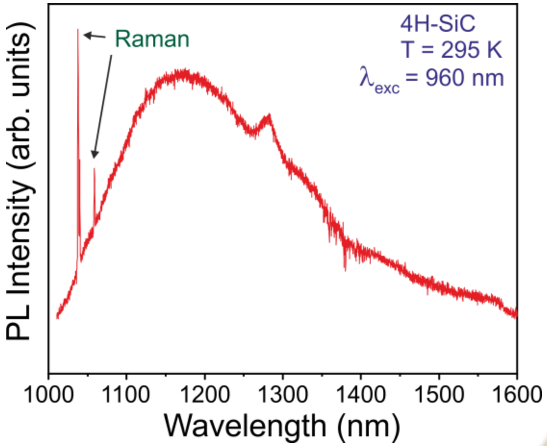
Full angular dependence



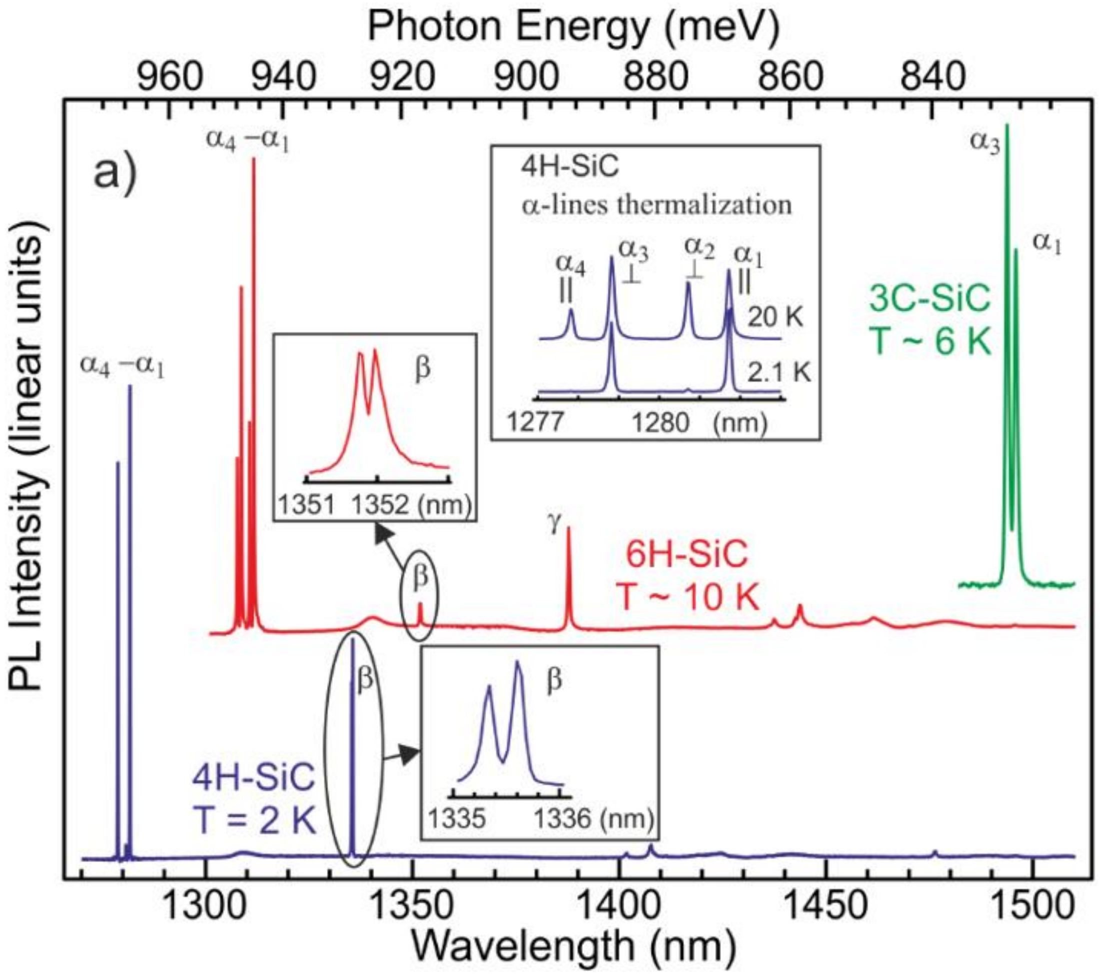
However, sample with stable divacancy emission is needed! (Fermi level near mid-bandgap).



Divacancy spectrum at room T

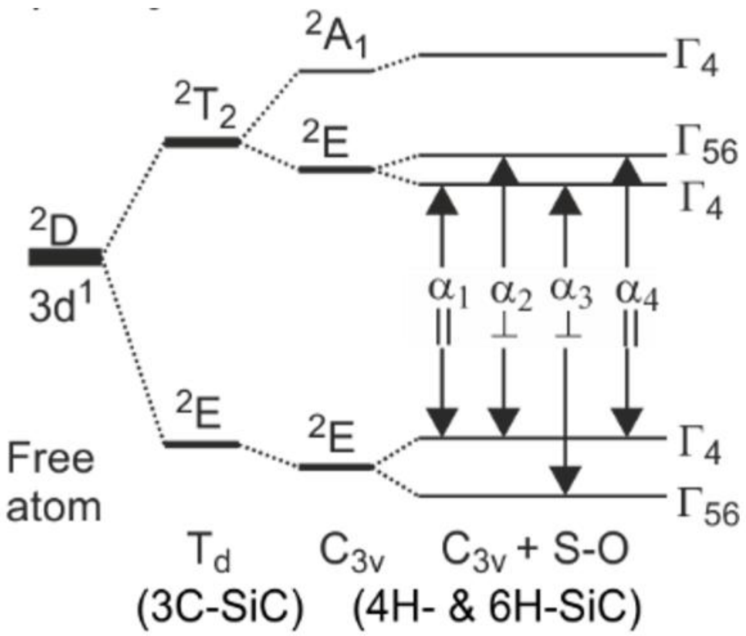


Vanadium (V) in SiC polytypes

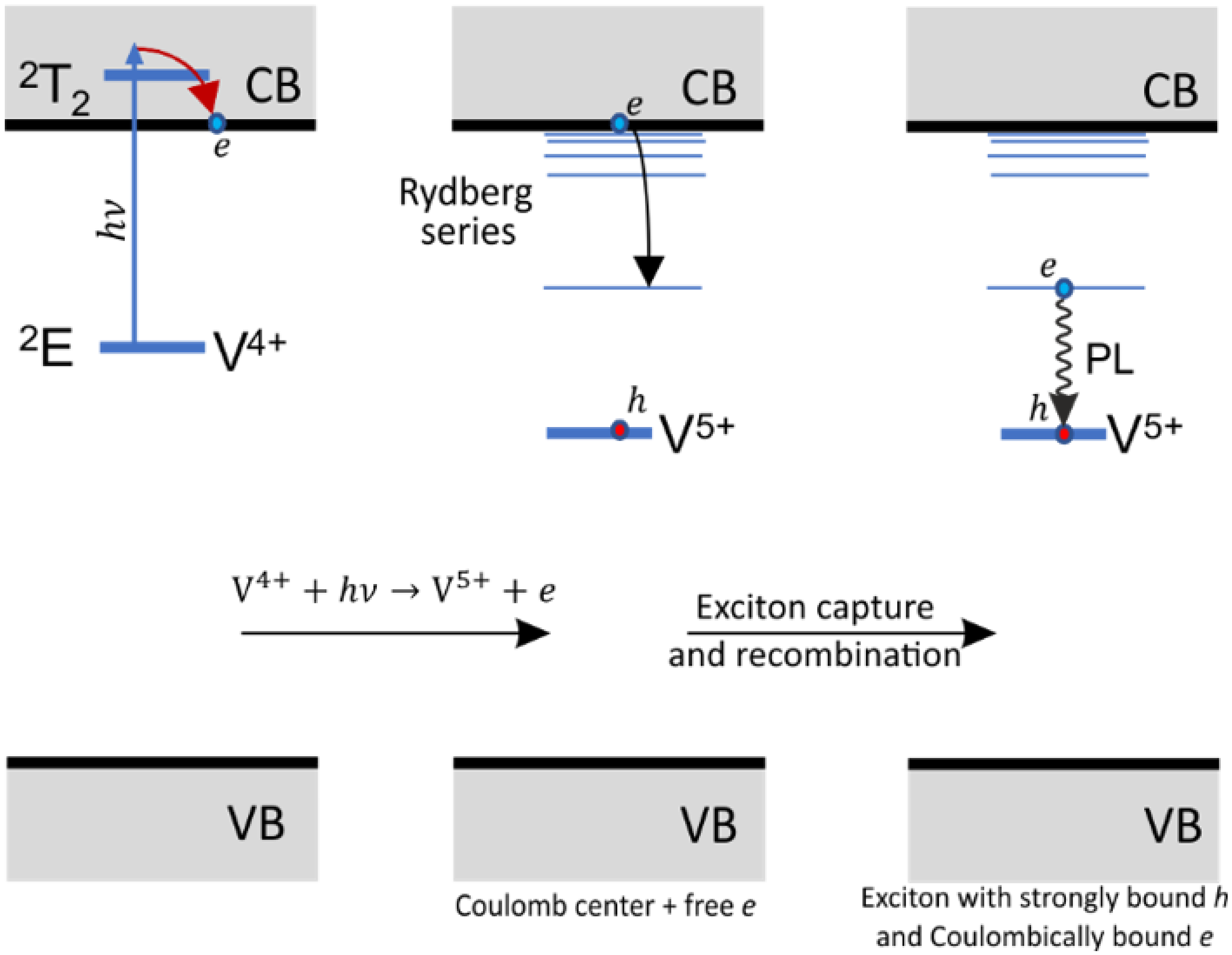


V: [Ar] $3d^3 4s^2$ (5 valence electrons)

Crystal-field model



Vanadium in 3C-SiC



The neutral V has spin S = 1/2.
Its usefulness for QT applications in 4H-SiC has been demonstrated [P. Cilibrizzi *et al.*, Nat. Commun. **14**, 8448 (2023)].

Can the defect in 3C-SiC be used in QT when it is a bound exciton instead of intra-atomic transition?