# Antisite pair recombination in SiC by a modified concerted exchange mechanism

related publication:

Posselt, M., Gao, F., Weber, W. J.,
*Atomistic simulations on the thermal stability of the antisite pair in 3C- and 4H-SiC,*
**Phys. Rev. B 73 (2006) 125206**


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# Motivation

## $D_I$ PL center:

- is observed at low temperature PL measurements, after electron, ion, or neutron irradiation, is found in as-grown material and in epitaxial layers, in *n* and *p* type material, in *3C*, *4H*, *6H* and *15R* polytypes

- is found to be stable after thermal treatment to above 2000 K

**$D_I$** (zero phonon) **lines**

*3C:* $L_1$ = 1.972 eV

*4H:* $L_1$ = 2.901 eV

*6H:* $L_1$ = 2.625 eV, $L_2$ = 2.600 eV, $L_3$ = 2.570 eV

**band gap**

*3C*: 2.36 eV

*4H*: 3.23 eV

*6H*: 3.00 eV



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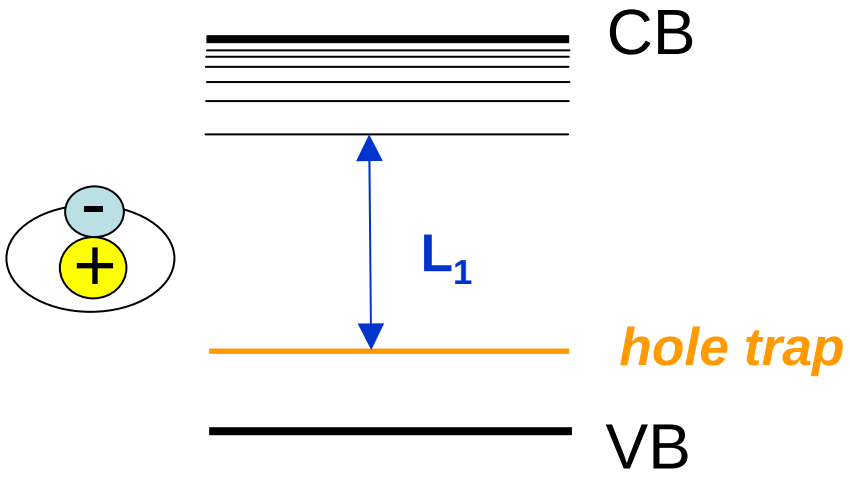
## *interpretation*

***Egilsson et al. 1999/2001 (4H-SiC):***

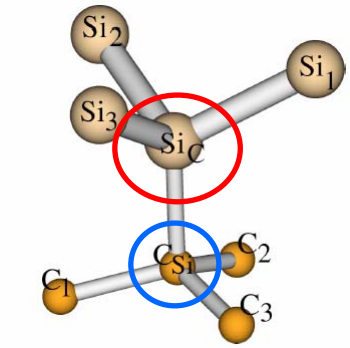
pseudo-donor model

exciton bound
to a **native defect**




- *native defect acts as a hole trap*
- *strongly localized hole captures an electron*
- *bound exciton is formed*
- *recombination between hole and electron gives the $L_1$ emission line*

## candidates for the native defect:

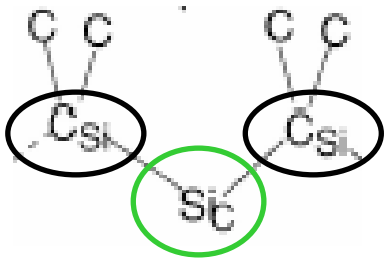



***Eberlein et al. 2002:***

***Gali et al. 2003:***

**first-neighbor antisite pair $Si_C C_{Si}$**

***Pinheiro, Rauls et al. 2004/2005:*** **$Si_C(C_{Si})_2$ complex**




***however:***

**calculation of spectra is based on the existence of $Si_C C_{Si}$ and $Si_C(C_{Si})_2$, their thermal stability has not yet been checked**

***this work:*** **dynamic simulations on the thermal stability of $Si_C C_{Si}$ in *3C*- and *4H-SiC***

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# Simulation method

## systematic classical MD simulations

- interatomic potential of Gao et al.
- supercell with 1152 (*3C-SiC*) or 1920 (*4H-SiC*) atoms

## ab-initio MD simulations for selected examples

- DFT-code NWCHEM
- supercell with 128 atoms (*3C-SiC*)


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## *determination of the thermal stability of $Si_CC_{Si}$:*

- **system with $Si_CC_{Si}$ is heated rapidly to a given temperature**

- **lifetime of $Si_CC_{Si}$ and the atomic recombination mechanism are analyzed by different independent methods**

- **due to the statistical nature of the recombination process, several statistically independent simulations must be performed at each temperature**


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## *accuracy of the interatomic potential of Gao et al:*

**V and I formation energies and migration barriers agree reasonably well with results of ab-initio calculations**

**structure and energetics of the antisite pair are also in good agreement with data obtained by ab-initio methods**


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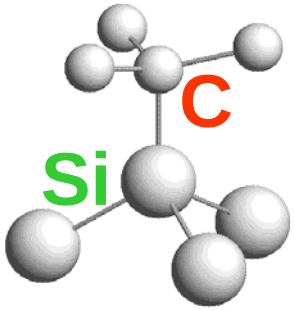
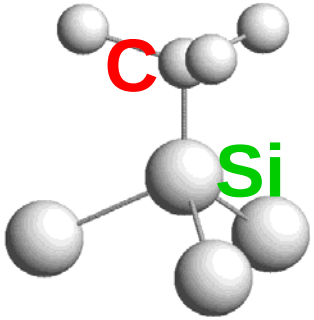
# *antisite pair configurations in 3C- and 4H-SiC*

## *3C-SiC*

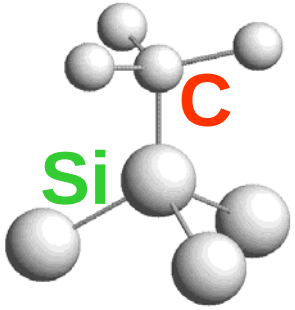



## *4H-SiC*

C and Si on hexagonal sites (1)




C and Si on cubic sites (1), mixed configuration (2)




| | CP | | | SCC-DFTB | DF | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reference | **this work** | | | Rauls *et al.* 2001 | Wang *et al.* 1988 | Torpo *et al.* 1999 | Eberlein *et al.* 2002 | | Gali *et al.* 2003 | Gali *et al.* 2003 |
| | **3C-SiC** | **4H-SiC, atoms on two hexagonal sites** | **4H-SiC, other configurations** | 4H-SiC, ∥c, atoms on two cubic sites | 3C-SiC | 3C-SiC | 4H-SiC, ∥c | 4H-SiC, not ∥c | 3C-SiC | 4H-SiC |
| formation energy (eV) | **6.65** | **6.72** | **6.66** | 5.2 | 5.9 | 5.8 | 5.68 | 5.33 | 6.1 | 5.9 |
| binding energy (eV) | **2.82** | **2.75** | **2.83** | 2.5 | 2.5 | 2.49 | 2.07 | 2.42 | | |
| Si-C bond length | **-3%** | **-4%** | **-3%** | -2% | | -2% | | | | |
| C-C bond length | **-10%** | **-10%** | **-10%** | -12% | | -12% | | | | |
| Si-Si bond length | **+24%** | **+27%** | **+24%** | +15% | | +16% | | | | |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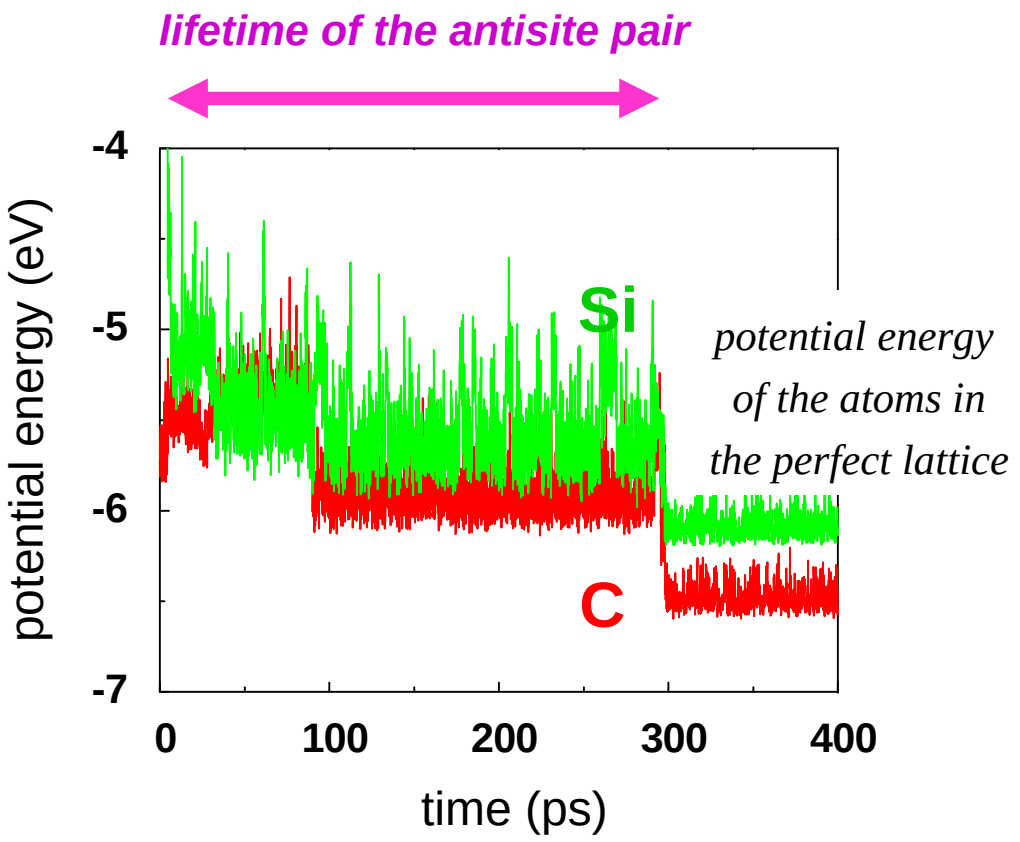
# Results for *3C-SiC*

The antisite pair recombination was studied at eleven temperatures between 800 and 2500 K (10 statistically independent simulations at each temperature).

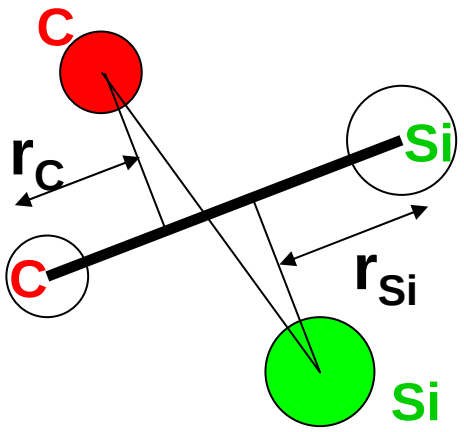
***example: T = 1000 K***

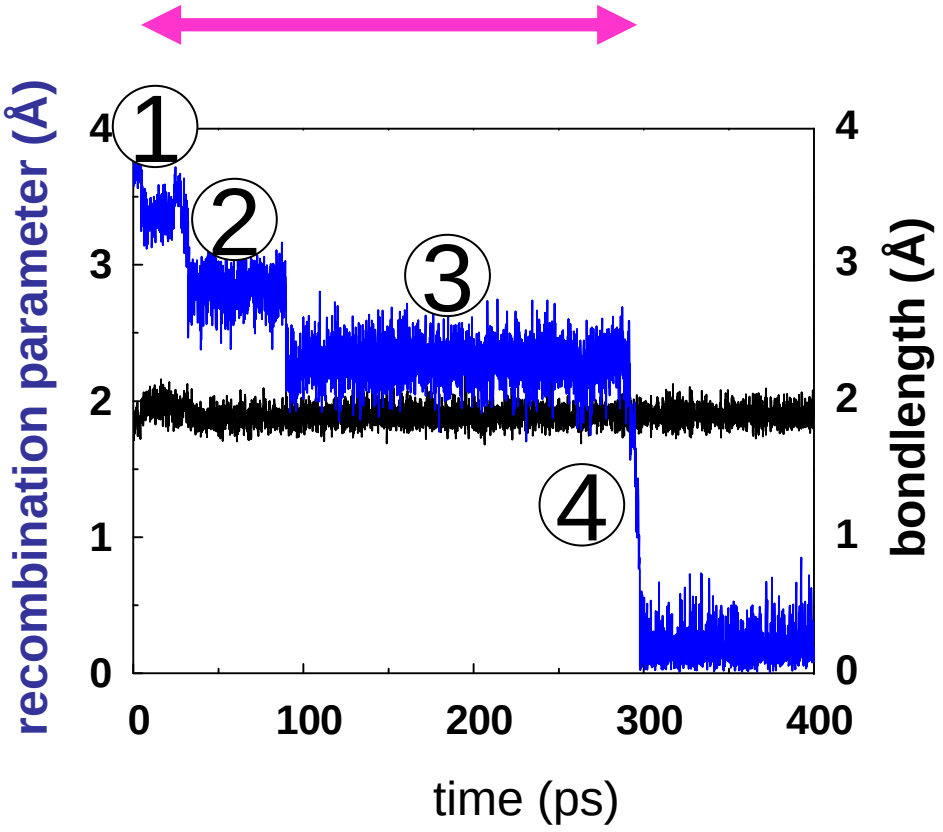
**evolution of the potential energy of the two atoms of the antisite pair**



# time dependence of the recombination parameter (rp) and evolution of the bond length between the atoms of the antisite pair

$$rp = r_c + r_{Si}$$




**antisite pair recombination consists of 4 stages**



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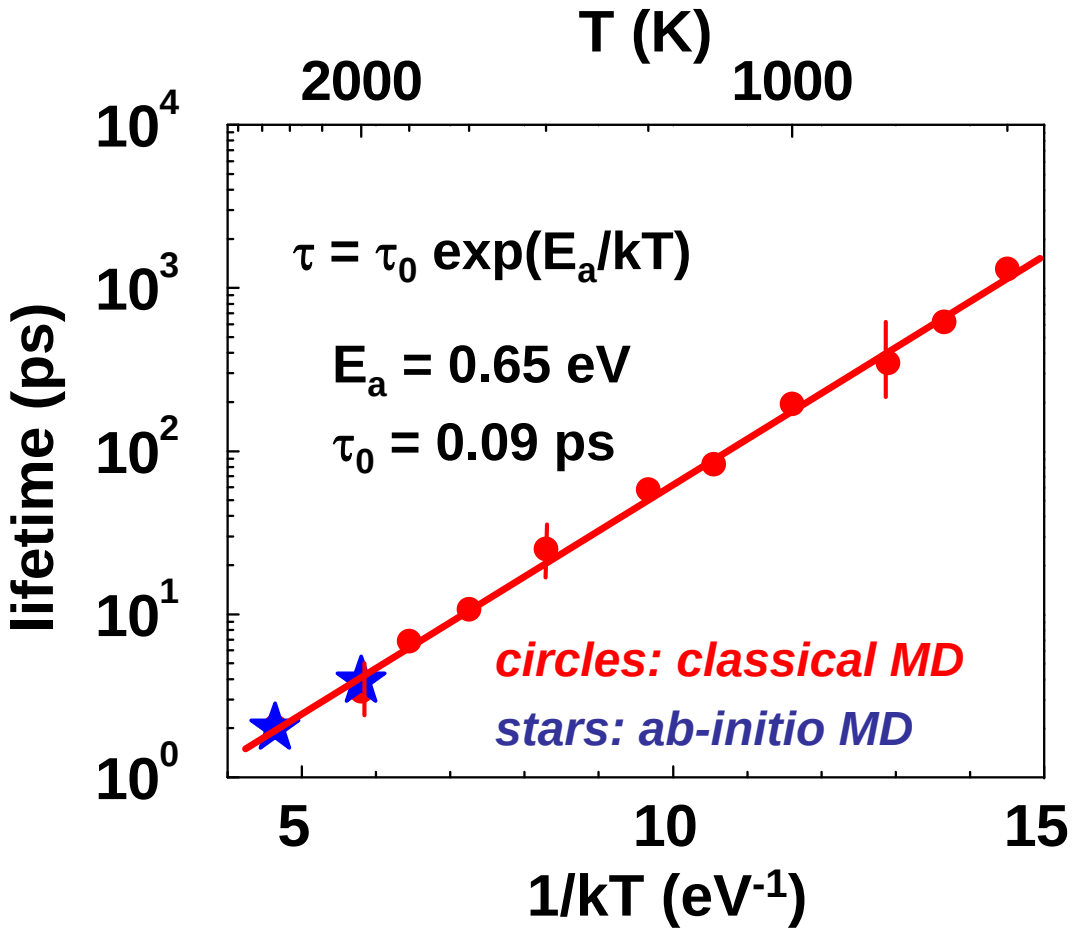
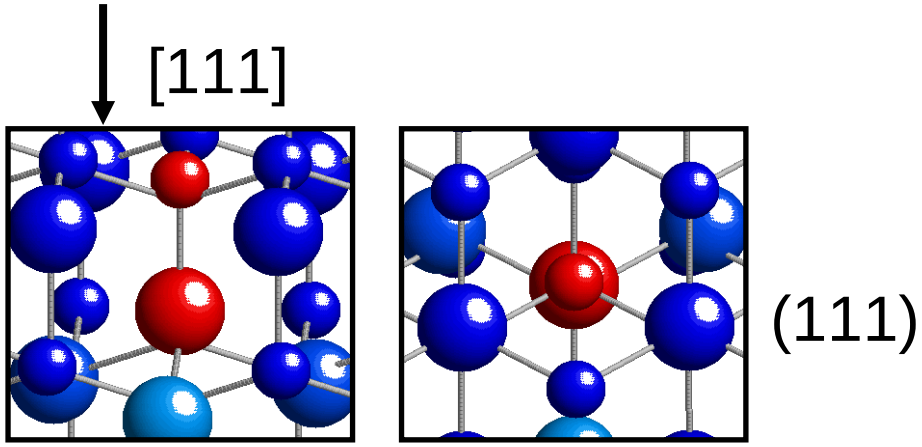



**In *3C-SiC* the thermal stability of the antisite pair is low. It can be therefore *not* correlated with the $D_I$ PL center that is stable up to 2000 K.**

# modified concerted exchange mechanism

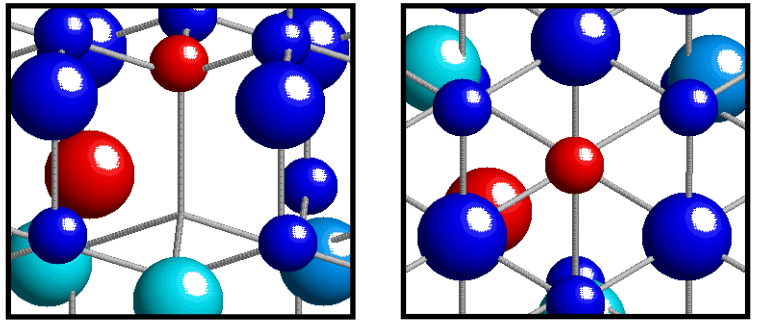
***found by the visualization of the MD data***

**antisite pair** near (-1-12)




1

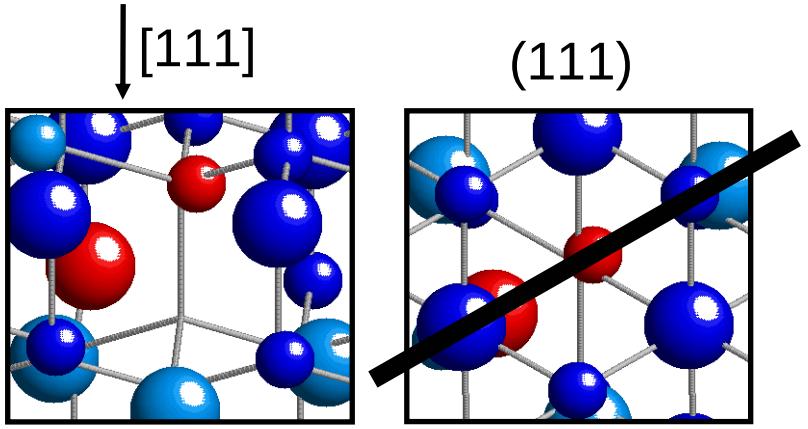
***Si moves to a position close to a tetrahedral site***



$V_C+Si_{TC}+C_{Si}$

2

*configuration changes slightly, but remains in a {110} plane*




$V_C+Si_{TC}+C_{Si}$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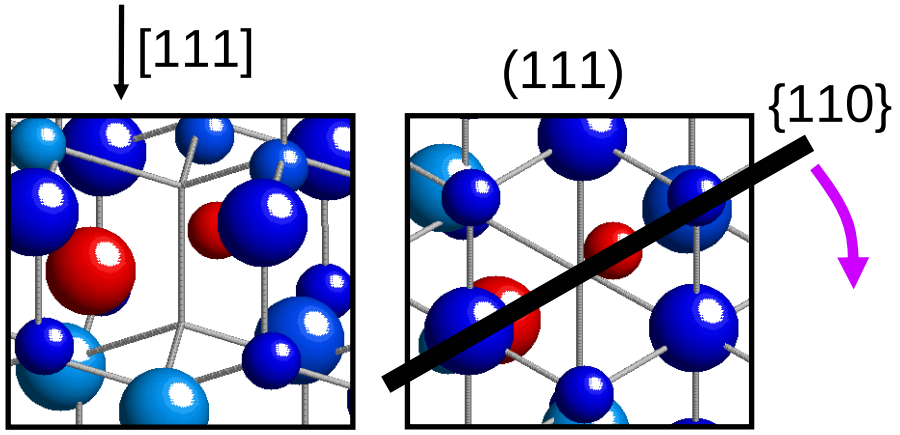
3

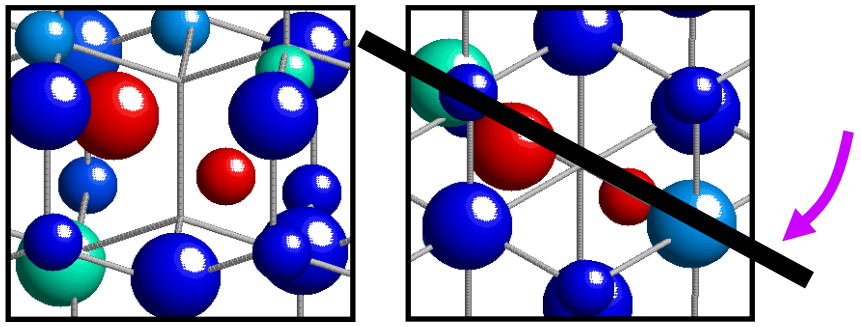
*rotation of the Si –C pair in the {110} plane*




bond defect, type 1

4

*further rotation of the Si –C pair, gradual change of the rotation plane until another {110} plane is reached*



bond defect, type 2



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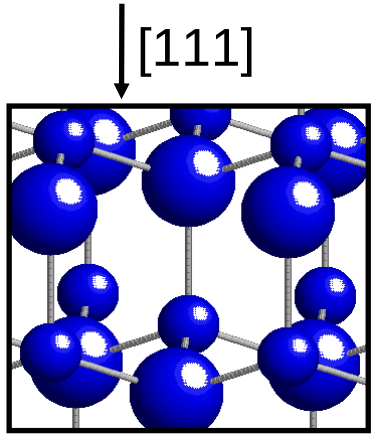
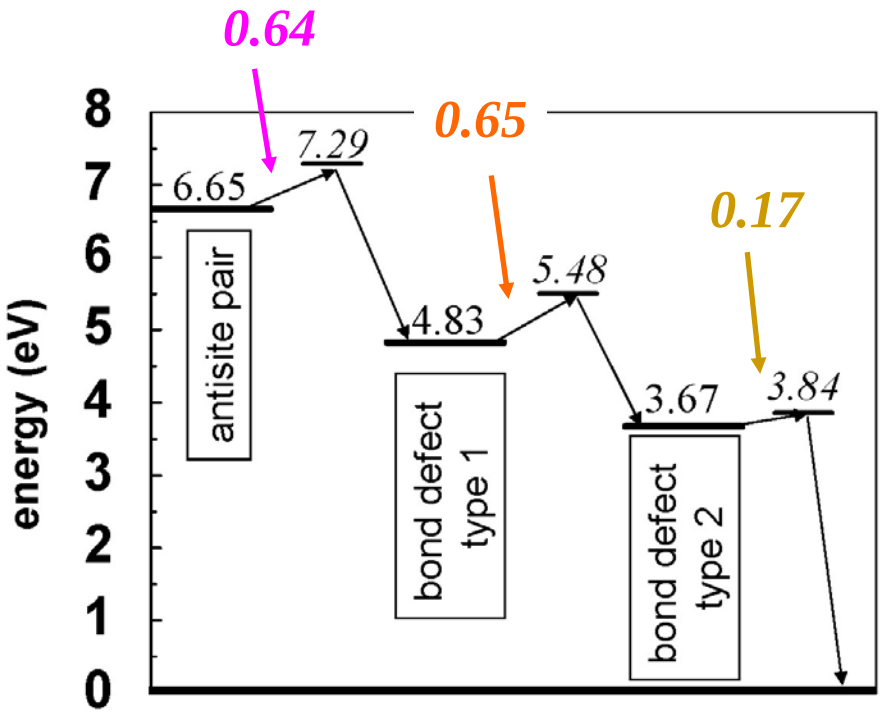
*rotation of the Si –C pair in the new {110} plane*

**perfect lattice**




*energetics of the modified concerted exchange*





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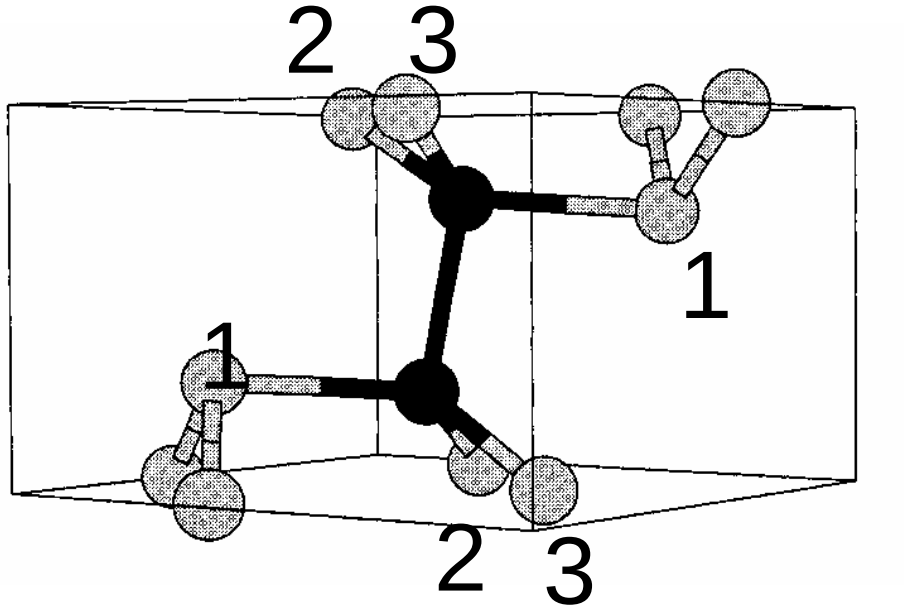
# bond defect in Si

*Tang et al.* *1997*

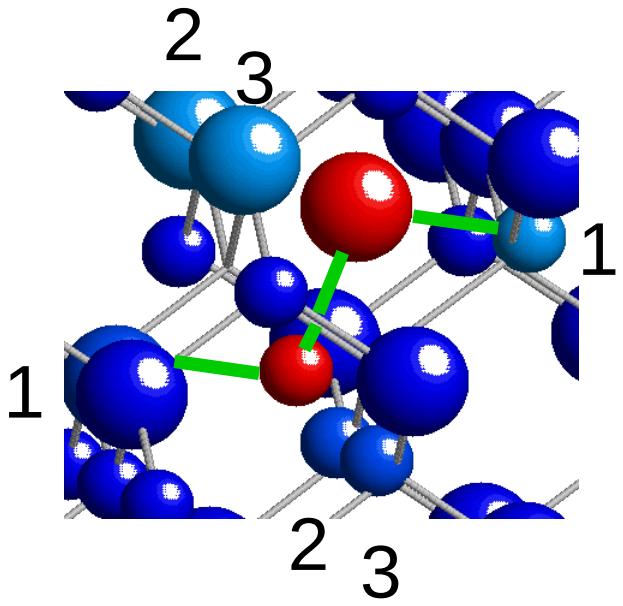
**result of incomplete V-I recombination**




all atoms are fourfold coordinated

# bond defects in *3C-SiC*

## bond defect, type 1

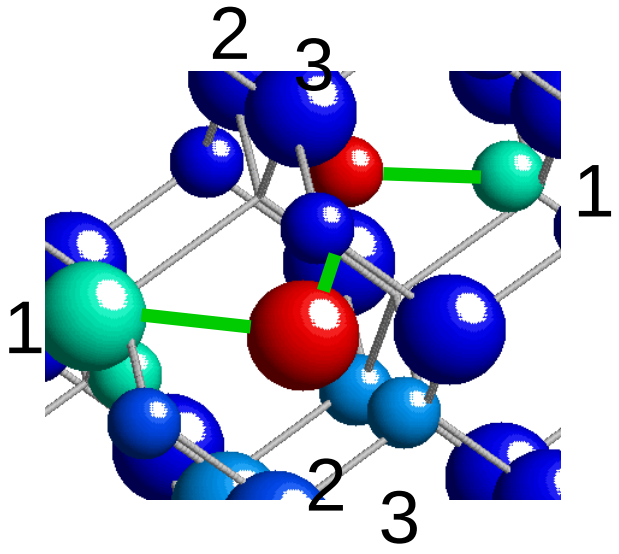



coordination of atoms: ~4

nearest neighbors of Si: **2 x Si, 2 x C**

nearest neighbors of C: **2 x Si, 2 x C**

## bond defect type 2

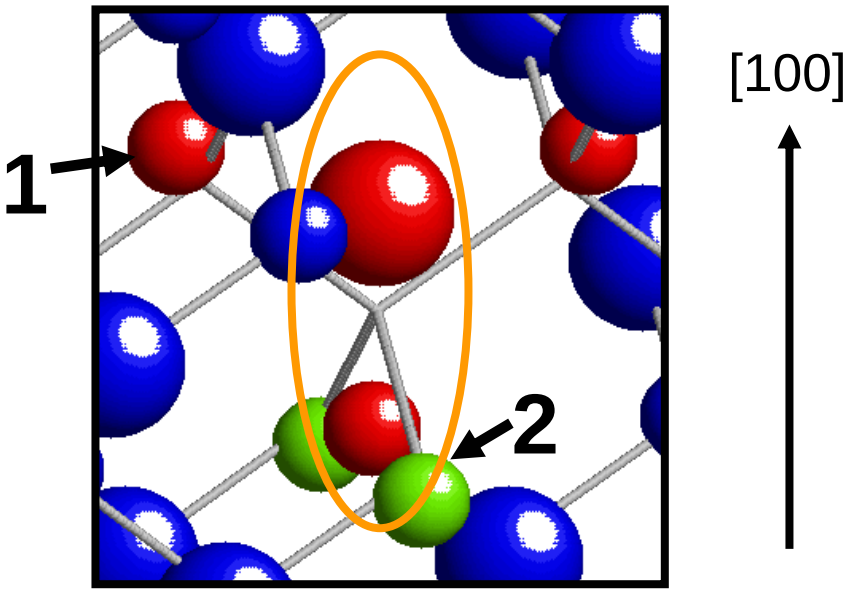



coordination of atoms: ~4

nearest neighbors of Si: **1 x Si, 3 x C**

nearest neighbors of C: **3 x Si, 1 x C**

<100>C+Si dumbbell




***Similarly to Si, the two bond defects in SiC can be considered as the result of incomplete recombination of $V_C$ and <100>C+Si.***

***This process is therefore one of the possible pathways for antisite pair formation.***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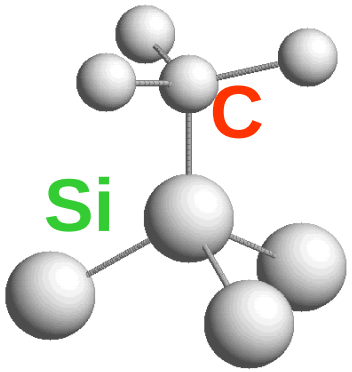
# Results for *4H-SiC*

The antisite pair recombination was studied at nine temperatures between 900 and 2000 K.

C and Si on cubic sites (1),
mixed configuration (2)




results are almost identical
to those for *3C-SiC*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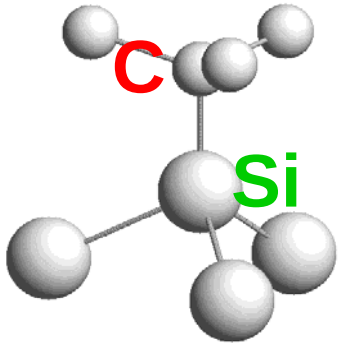
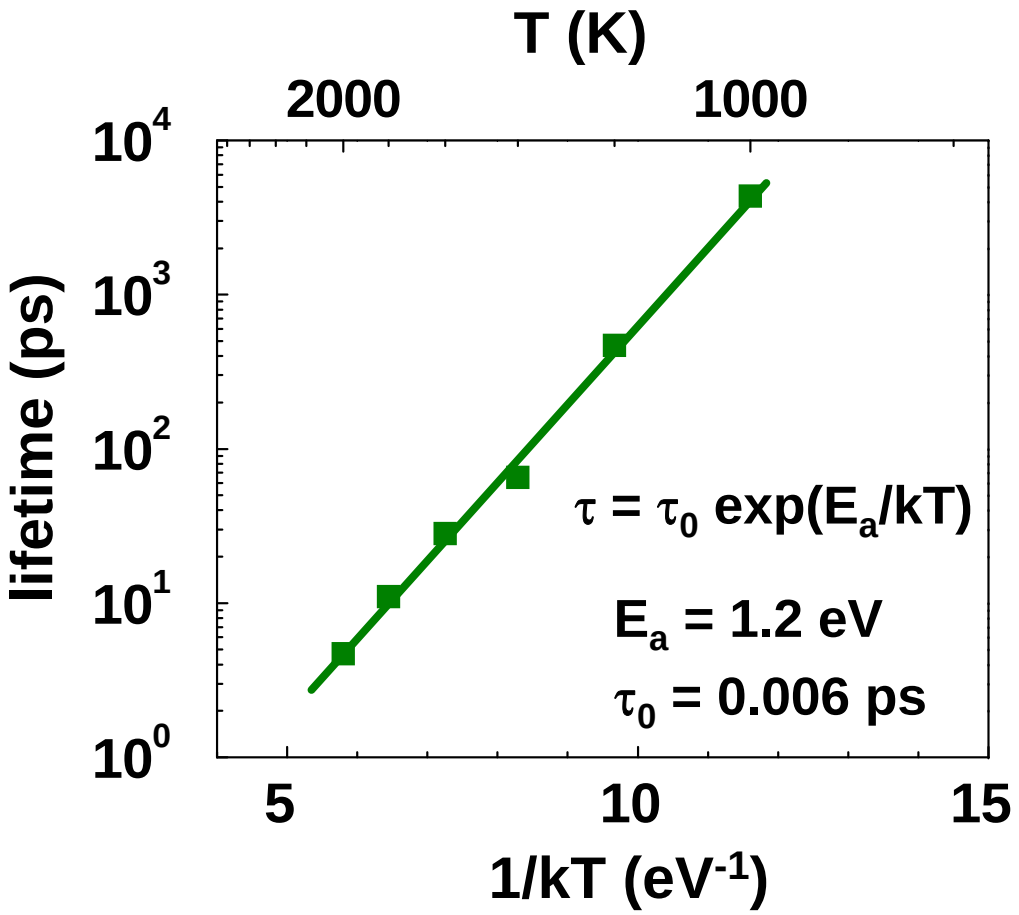
C and Si on hexagonal sites (1)



**The lifetime of the antisite pair with atoms on hexagonal sites is different to that of the three other types of antisite pairs.**

***The recombination mechanism is <u>not</u> a concerted exchange.***
***It is rather characterized by the separate motion of the atoms.***
***Two reaction paths were identified:***

***(i) main path: only the two atoms of the antisite pair move significantly.***

***(ii) other path: motion of more than two atoms.***

**In *4H-SiC* the thermal stability of the four types of antisite pairs is low. They can be therefore *<u>not</u>* correlated with the $D_I$ PL center that is stable up to 2000 K.**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# Summary

- The thermal stability of the antisite pair in *3C*- and *4H-SiC* is low. Therefore, it is not a candidate for the $D_I$ PL center.

- The recombination of the antisite pair in *3C-SiC* and of three antisite pair configurations in *4H-SiC* occur via a modified concerted exchange, with two types of bond defects as intermediate states.


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