

Hydrogen interaction with vacancies in Ti

Petr Hruška¹, Jakub Čížek¹, Jan Knapp¹, Oksana Melikhova¹,
Silvie Mašková¹, Ladislav Havela¹, František Lukáč¹

¹Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic



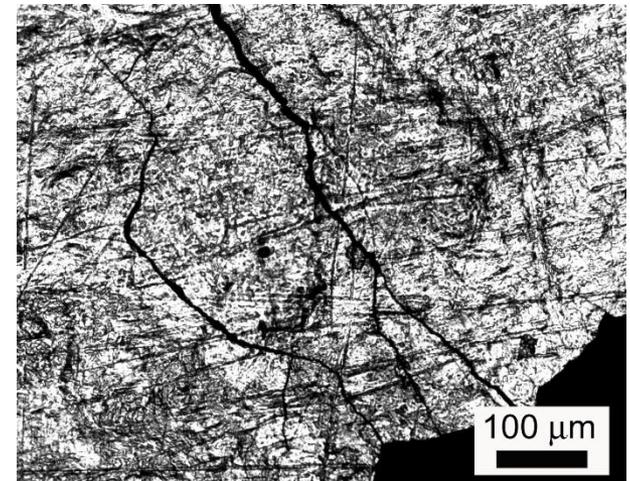
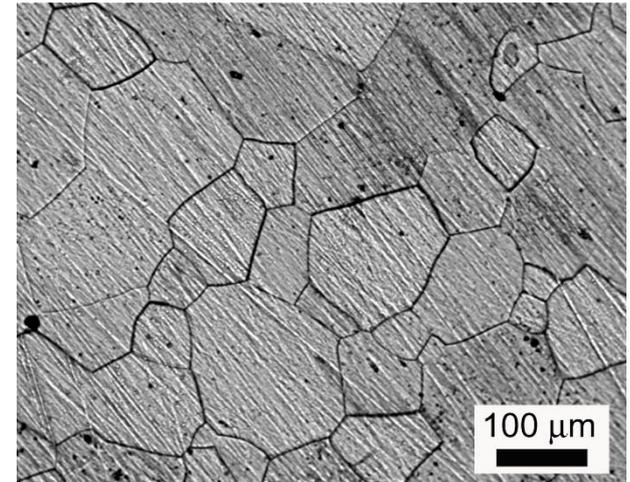
Hydrogen and defects in Ti

Ti and Ti-based alloys are attractive materials for its mechanical properties (high strength-to-weight ratio, corrosion resistance...).

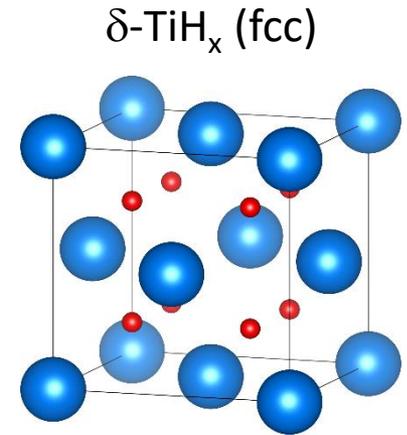
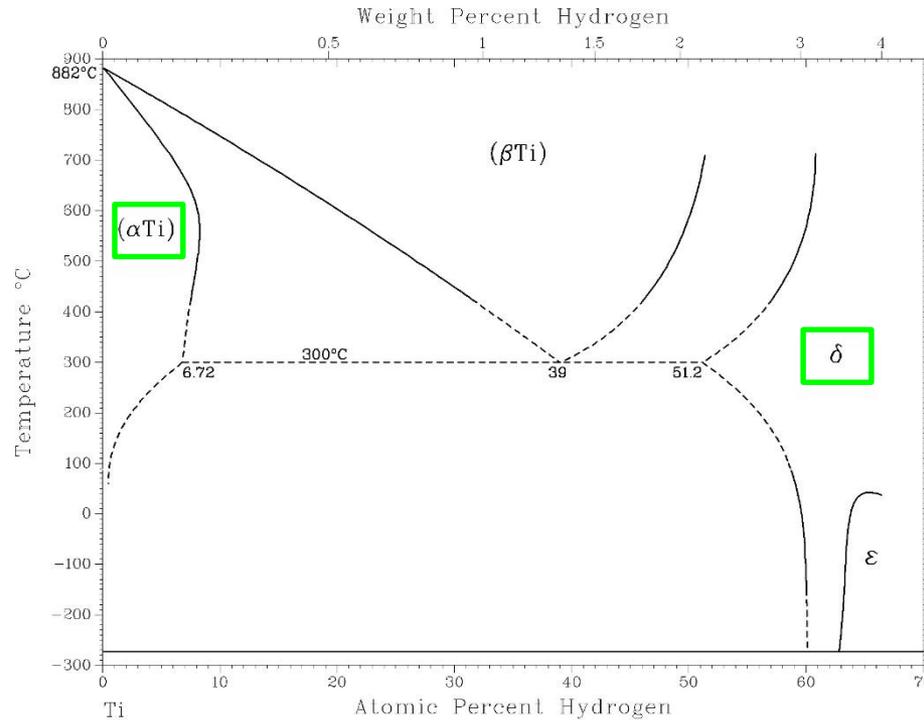
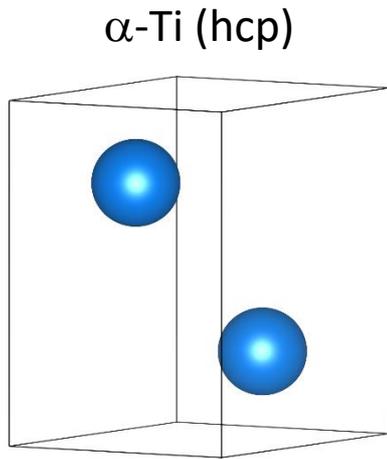
In many applications they are **exposed to hydrogen** containing environment.

There is an attractive interaction between vacancy and hydrogen atom. The **formation energy is lower for v+H complex** than for empty vacancy. The equilibrium vacancy concentration is enhanced.

Hydrogen-induced defects lead to degradation of mechanical properties of Ti (**Hydrogen assisted cracking** = HAC). In order to elucidate the mechanism of HAC the study of interaction of hydrogen with defects in Ti is required.



Ti-H system



“low temperature” titanium
H in interstitial sites

hydride phase TiH_x
 $1.5 < x \leq 2$

Ab-initio DFT calculations

Density functional theorem (DFT) theoretical modeling by VASP program [1] using projected augmented waves pseudo-potentials [2].

The electron exchange potential was treated with the Perdew-Wang **generalized gradient approximation** (GGA) [3].

Plane-wave energy cut-off was fixed to 400 eV.

The Brillouin zone was sampled by $4 \times 4 \times 4$ k -point mesh generated using the Monkhorst–Pack scheme [4].

The structural optimization (lattice relaxation) was stopped when the forces converged to less than 0.01 eV/\AA .

[1] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.

[2] G. Kresse, D. Joubert Phys. Rev. B 59 (1999) 1758.

[3] Y. Wang, J.P. Perdew, Phys. Rev. B 44 (1991) 13298.

[4] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 13 (1976) 5188.

Ti supercell

N = 216 Ti atoms

hcp α -Ti lattice

lattice parameters: $a = 2.95 \text{ \AA}$

$c = 4.68 \text{ \AA}$

central Ti ion removed

→ Ti vacancy

decoration of vacancy with n H atoms
in tetrahedral sites

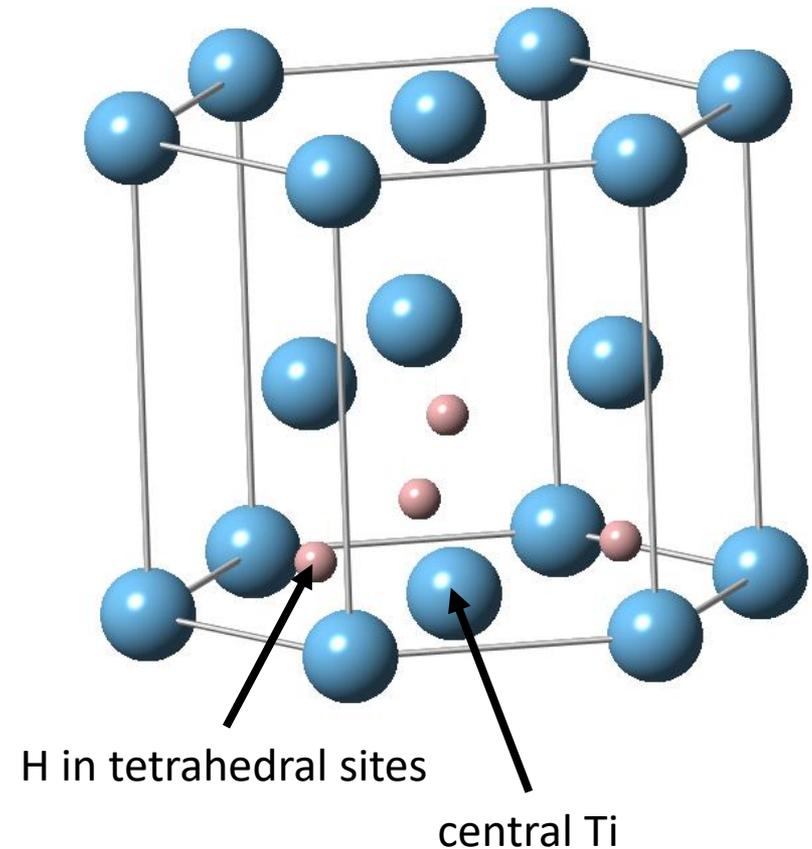
→ v+nH complexes

minimal energy configuration

→ inward/outward lattice relaxation

zero-point energy (ZPE) of H atoms

→ ground state vibration energy



Hydrogen interstitials in Ti

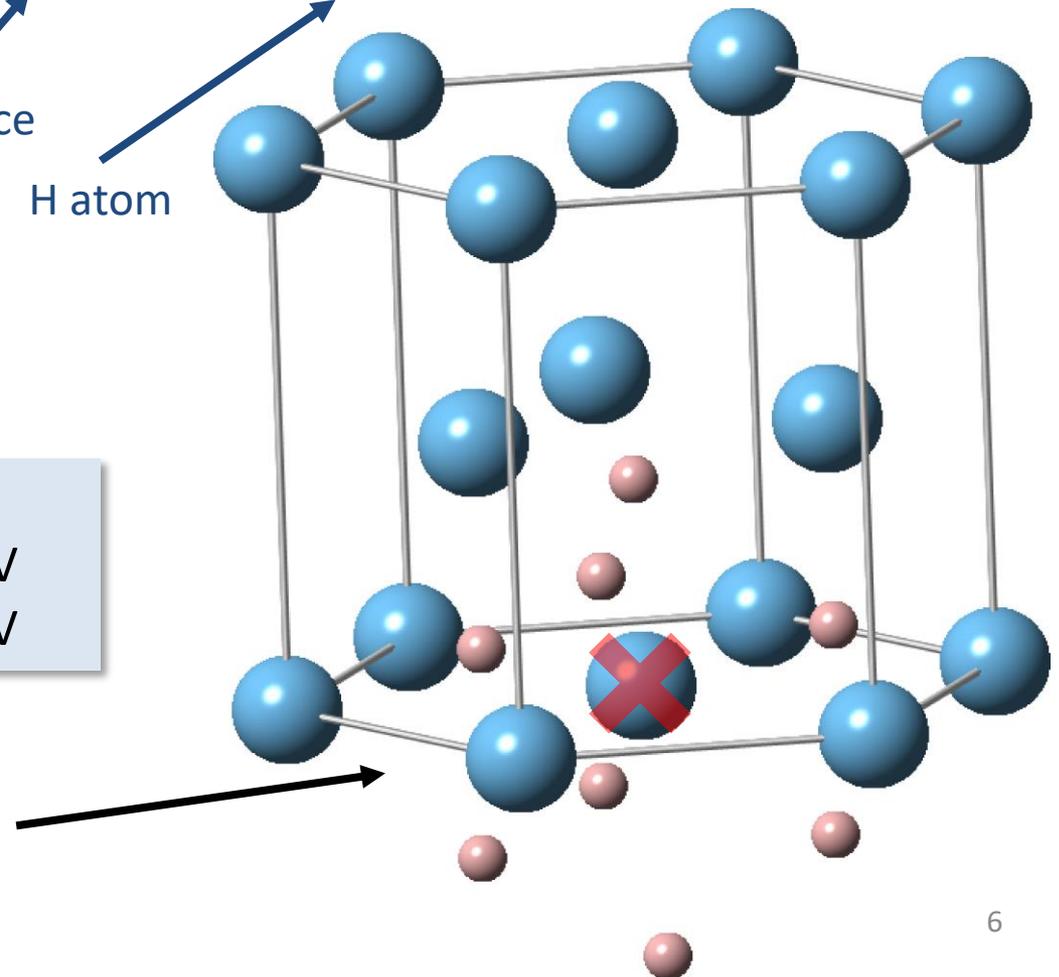
$$E_{f,H_i} = E(H_i) + ZPE(H_i) - E(\text{bulk}) - \frac{1}{2}(E(H_2) + ZPE(H_2))$$

H insertion energy (black arrow pointing to E_{f,H_i})
 Ti lattice with H interstitial (red arrow pointing to $E(H_i)$)
 ZPE of H interstitial (red arrow pointing to $ZPE(H_i)$)
 Ti lattice (blue arrow pointing to $E(\text{bulk})$)
 H atom (blue arrow pointing to $E(H_2)$)

H insertion energy in T-site:

calculated	$H_i = -0.49$ eV
measured	$H_i = -0.54$ eV

8 nearest neighbor interstitial tetrahedral sites around vacancy



Vacancy formation

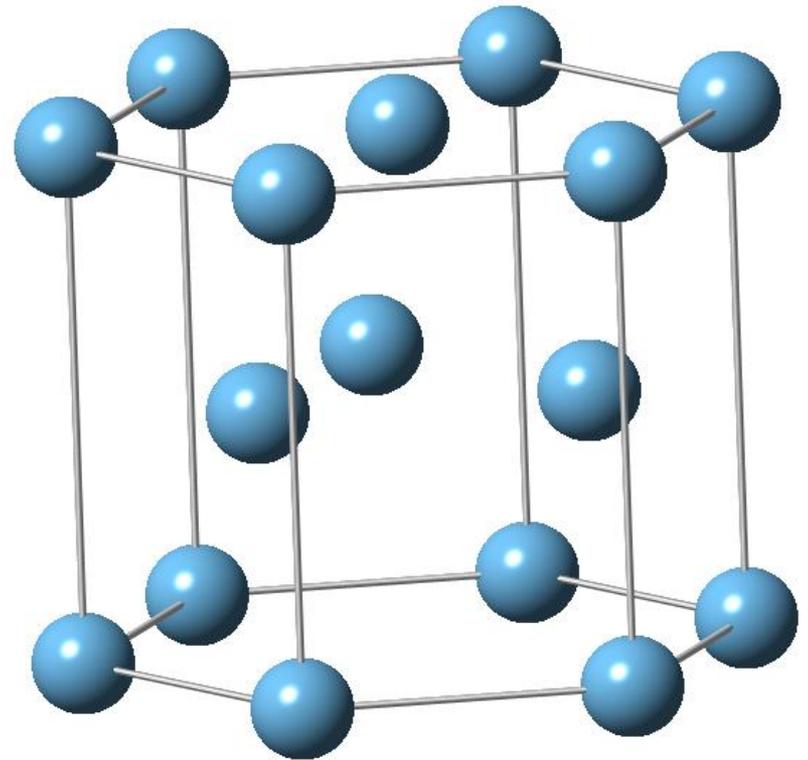
$$E_{f,v} = E(v) - \frac{N-1}{N} E(\text{bulk})$$

vacancy
formation
energy

Ti lattice
with vacancy

Ti lattice
without vacancy

our calculations: $E_f = 2.09 \text{ eV}$
previous studies: $E_f = 1.96 - 2.14 \text{ eV}$



Vacancy + hydrogen complex energies

$v+nH$ complex **formation energy** (formation of the complex in Ti lattice)

$$E_{f,v+nH} = E(v + nH) + ZPE(v + nH) - \frac{N-1}{N} E(\text{bulk}) - \frac{n}{2} (E(\text{H}_2) + ZPE(\text{H}_2))$$

$E(v + nH)$ and $ZPE(v + nH)$ are associated with the **Ti lattice with $v+nH$ complex**.
 $ZPE(v + nH)$ is also associated with the **ZPE of n H atoms**.
 $\frac{N-1}{N} E(\text{bulk})$ is associated with the **Ti lattice**.
 $\frac{n}{2} (E(\text{H}_2) + ZPE(\text{H}_2))$ is associated with **n H atoms**, which are represented as $n/2$ H_2 molecules. The energy of each H_2 molecule is the sum of $E(\text{H}_2)$ and $ZPE(\text{H}_2)$.

$v+nH$ complex **trapping energy** (trapping of interstitial H atom by $v+(n-1)H$ complex)

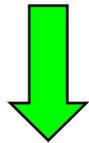
$$E_{t,v+nH} = E(v + (n-1)H) + ZPE(v + (n-1)H) + E(\text{H}_i) + ZPE(\text{H}_i) - E(\text{bulk}) - E(v + nH) + ZPE(v + nH)$$

$E(v + (n-1)H) + ZPE(v + (n-1)H)$ is associated with the **Ti lattice with $v+(n-1)H$ complex**.
 $E(\text{H}_i) + ZPE(\text{H}_i) - E(\text{bulk})$ is associated with the **interstitial H atom**.
 $-E(v + nH) + ZPE(v + nH)$ is associated with the **Ti lattice with $v+nH$ complex**.

v+1H complex

H atom displaced towards the vacancy.

trapping energy $E_t = -0.10$ eV

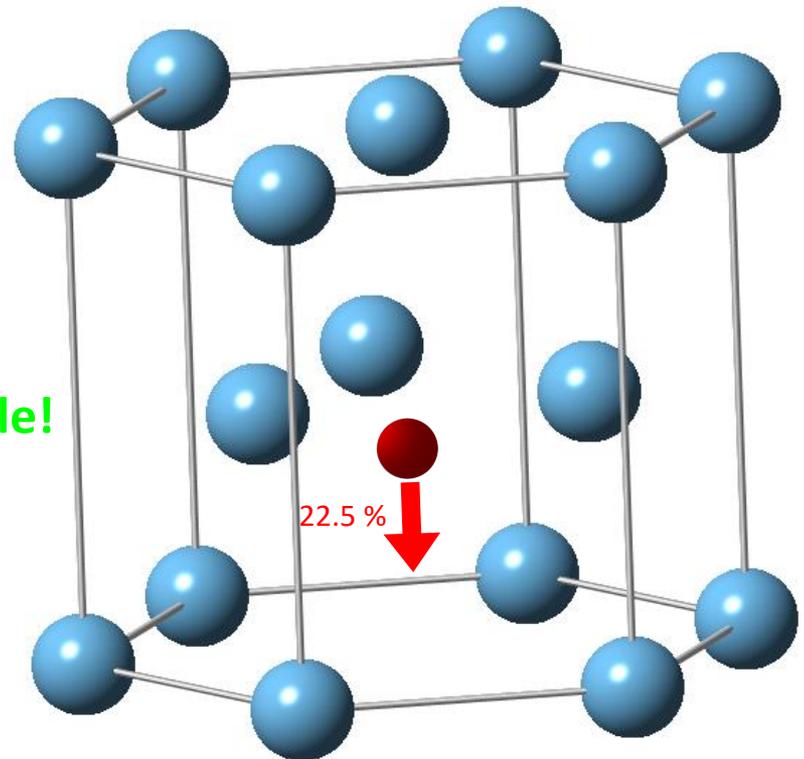


H trapping in vacancy is energetically favorable!

complex formation energy	$E_f = 1.88$ eV
vacancy formation energy	$E_f = 2.09$ eV

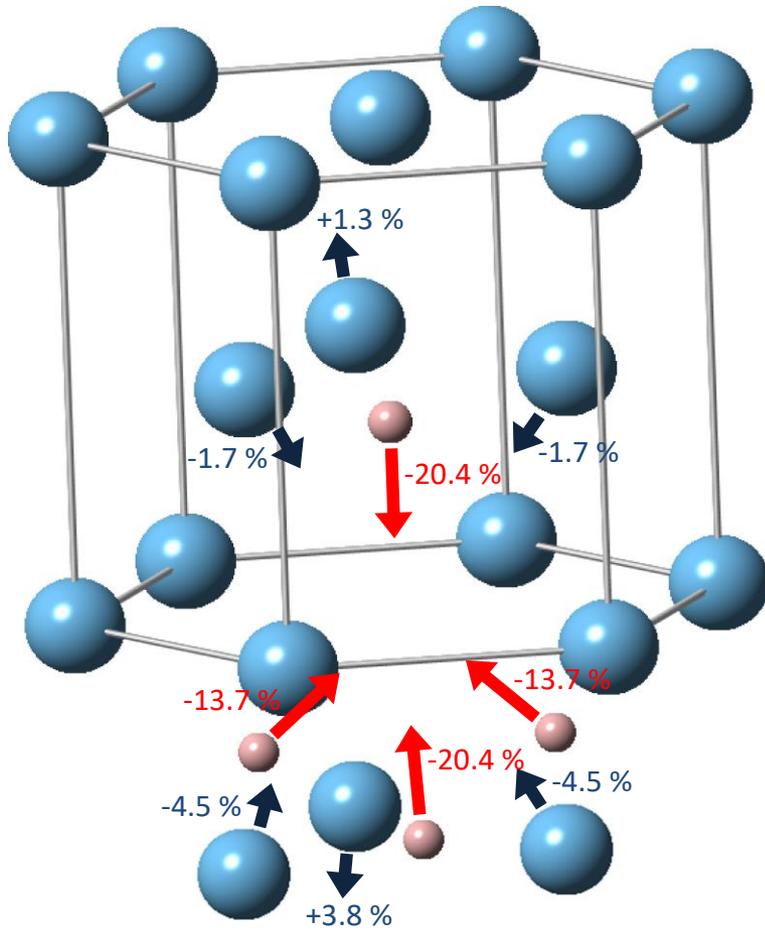


H reduces vacancy formation energy!



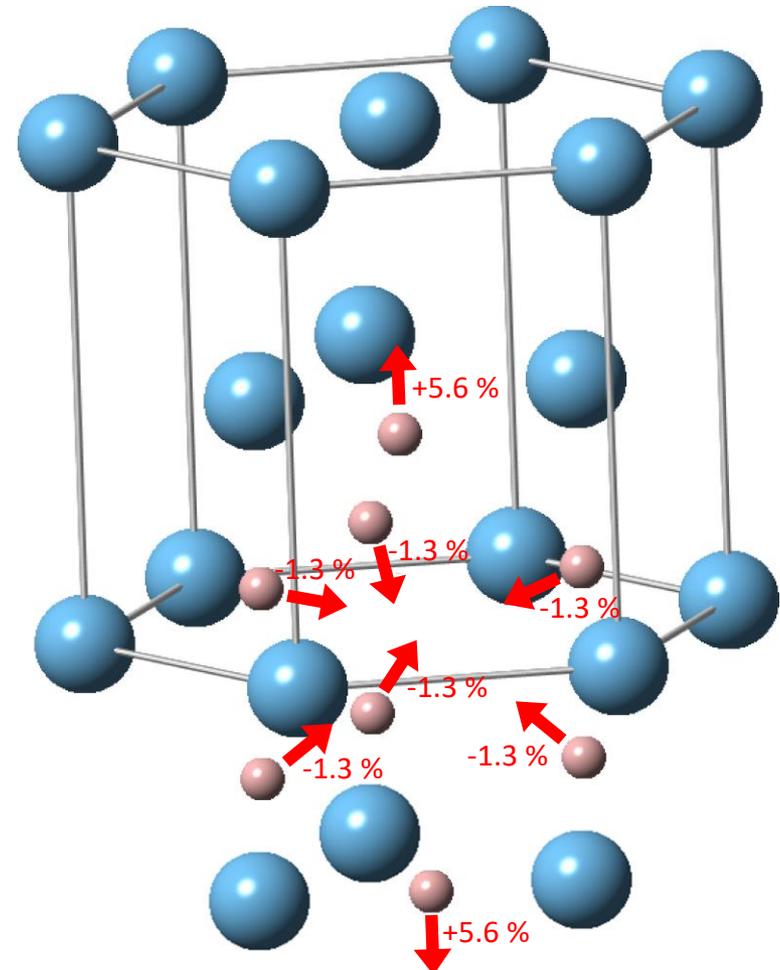
v+nH complexes (n = 4, n = 8)

v+4H complex



inward relaxation

v+8H complex



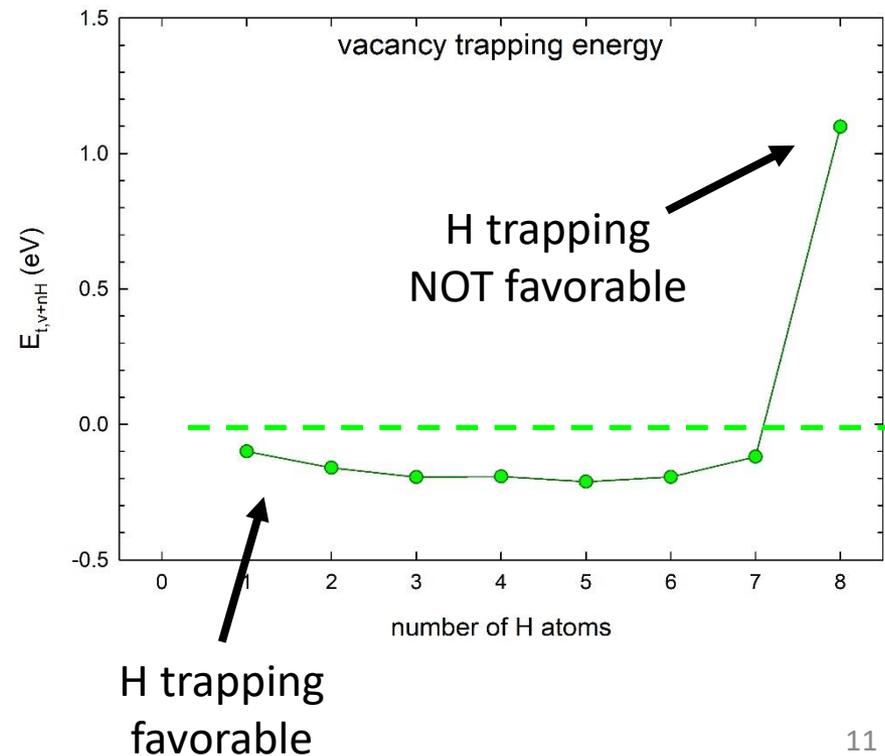
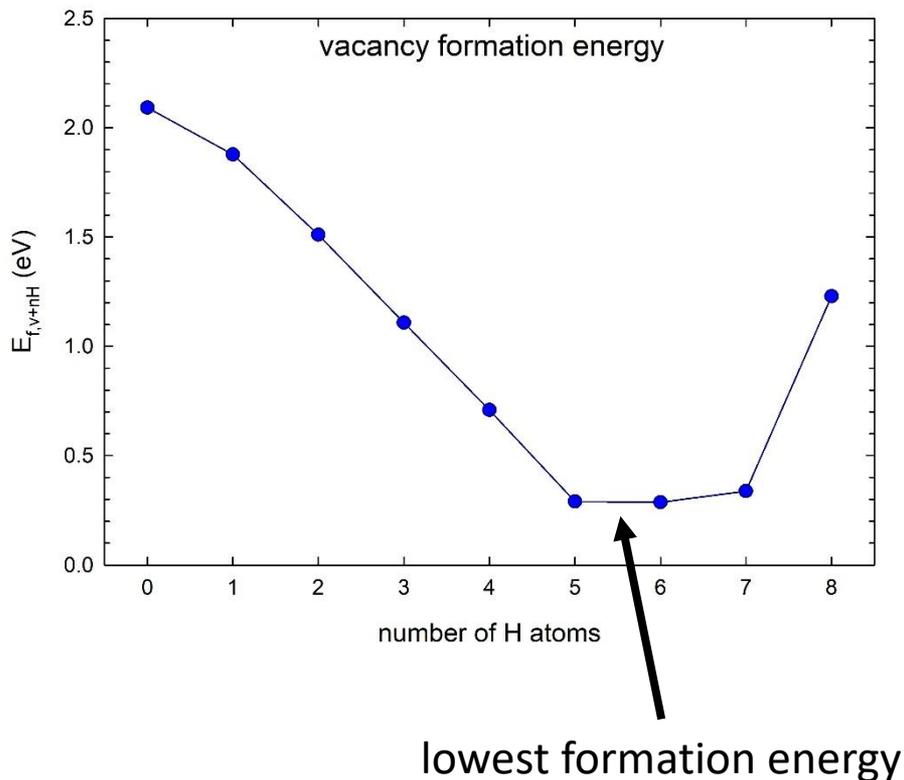
outward relaxation

v+nH complex – calculated energies

Vacancies are capable of trapping up to 7 H atoms.

The most energetically favorable configurations contain 5-7 atoms.

v+8H complex is energetically unstable and breaks up due to H-H repulsion.



Positron density and lifetime (standard scheme)

single particle Schrödinger equation for positron wave-function

$$-\frac{\hbar^2}{2m_0}\nabla^2\psi_+(\mathbf{r}) + V_C(\mathbf{r})\psi_+(\mathbf{r}) + V_X[n_-(\mathbf{r})]\psi_+(\mathbf{r}) = E_+\psi_+(\mathbf{r})$$

Coulomb potential of
electrons and nuclei

electron-positron correlation potential

positron lifetime

$$\frac{1}{\tau} = \pi r_e^2 c \int n_+(\mathbf{r})n_-(\mathbf{r})\gamma[n_-(\mathbf{r})]d\mathbf{r}$$

Local Density Approximation [1]

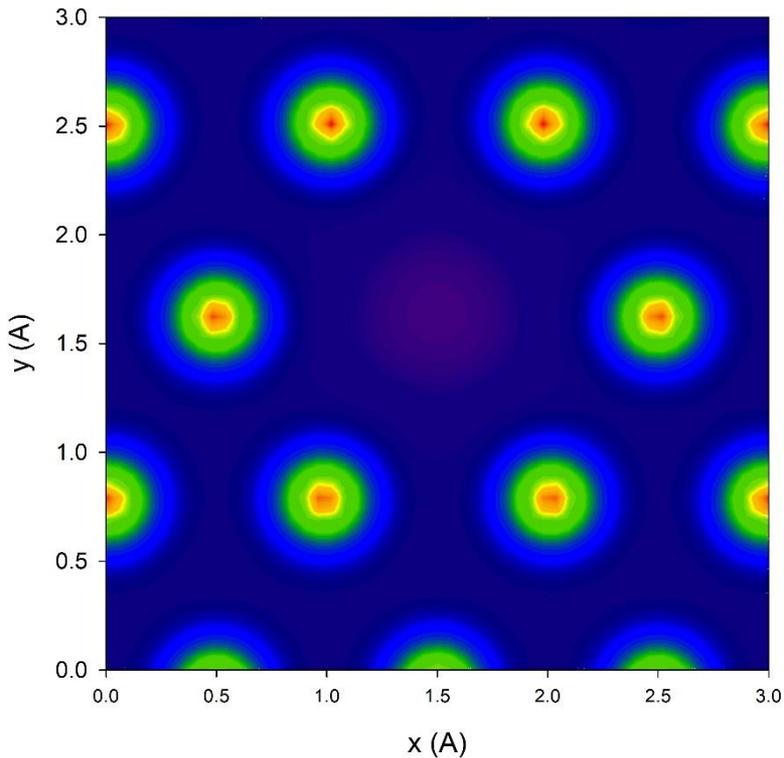
enhancement factor

Positron density – vacancy

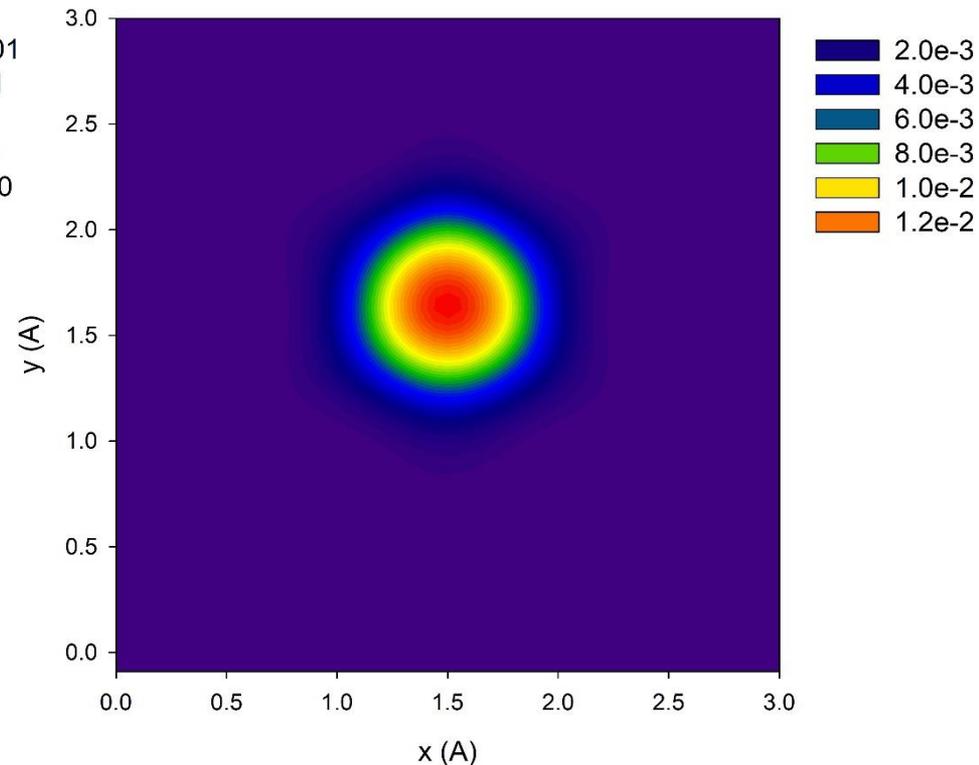
positron lifetime – overlap of electron and positron density

$$\frac{1}{\tau} = \pi r_e^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma[n_-(\mathbf{r})] d\mathbf{r}$$

electron density in basal (0001) plane



positron density in basal (0001) plane

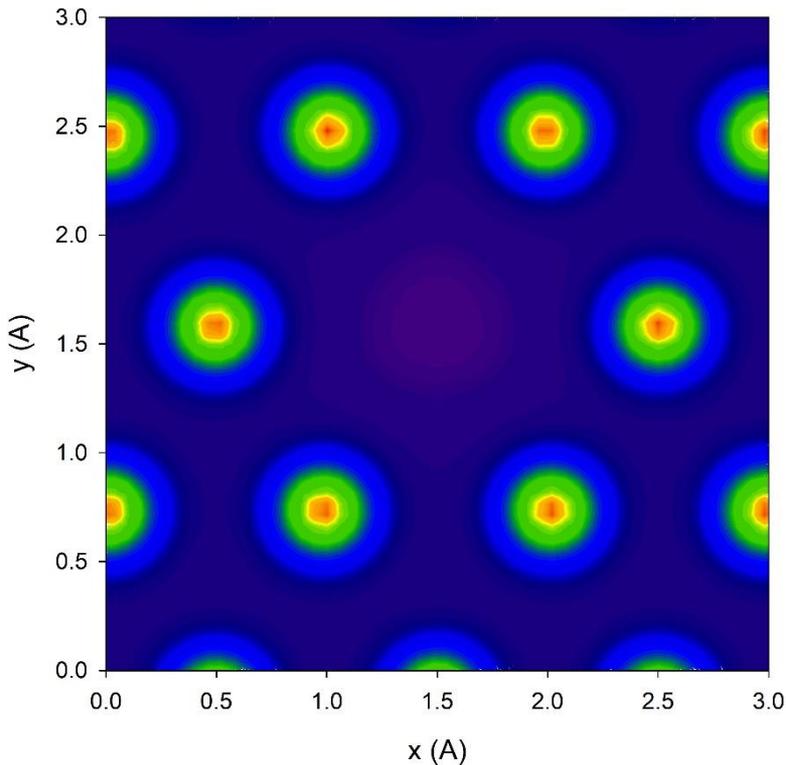


Positron density – v+H complex

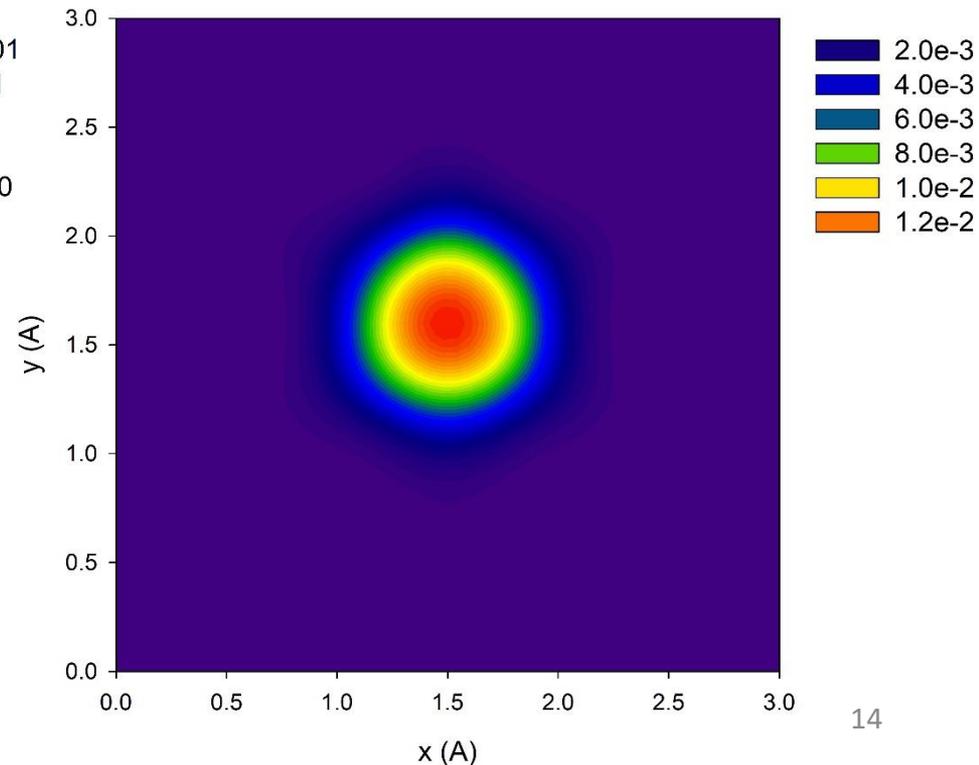
positron lifetime – overlap of electron and positron density

$$\frac{1}{\tau} = \pi r_e^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma[n_-(\mathbf{r})] d\mathbf{r}$$

electron density in basal (0001) plane



positron density in basal (0001) plane

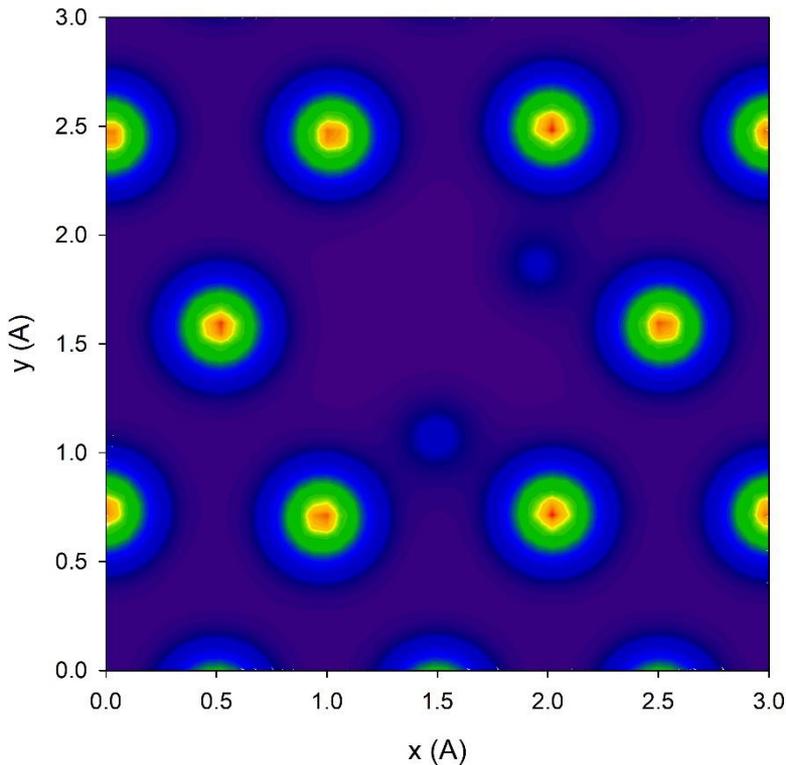


Positron density – v+4H complex

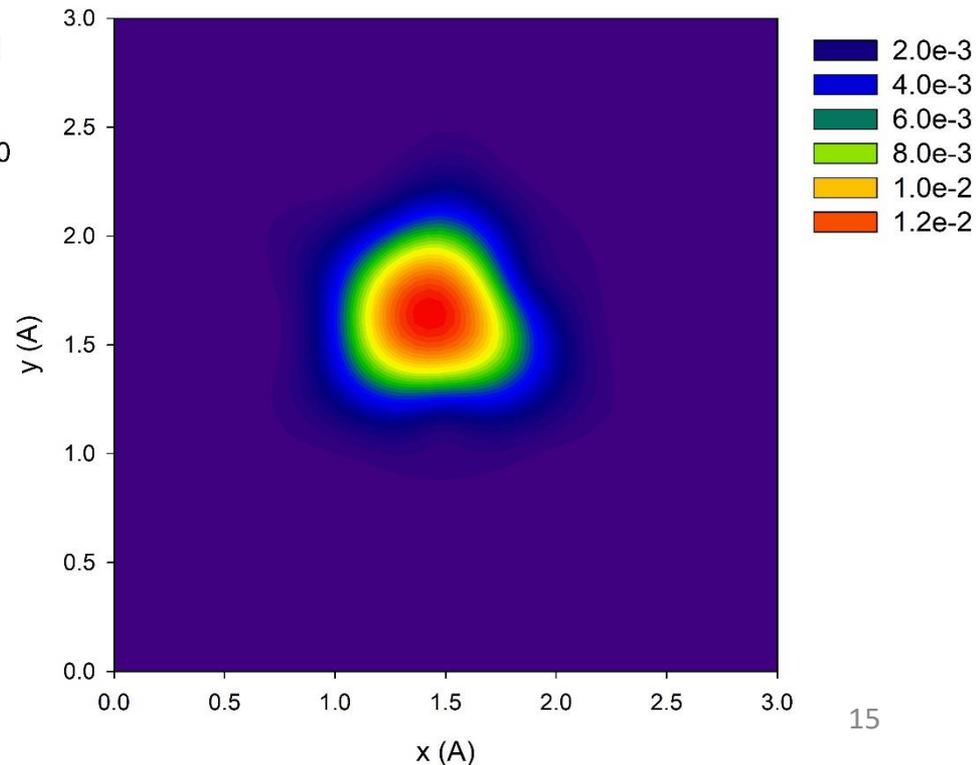
positron lifetime – overlap of electron and positron density

$$\frac{1}{\tau} = \pi r_e^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma[n_-(\mathbf{r})] d\mathbf{r}$$

electron density in basal (0001) plane



positron density in basal (0001) plane



Positron lifetime of v+nH complexes

non-relaxed lattice

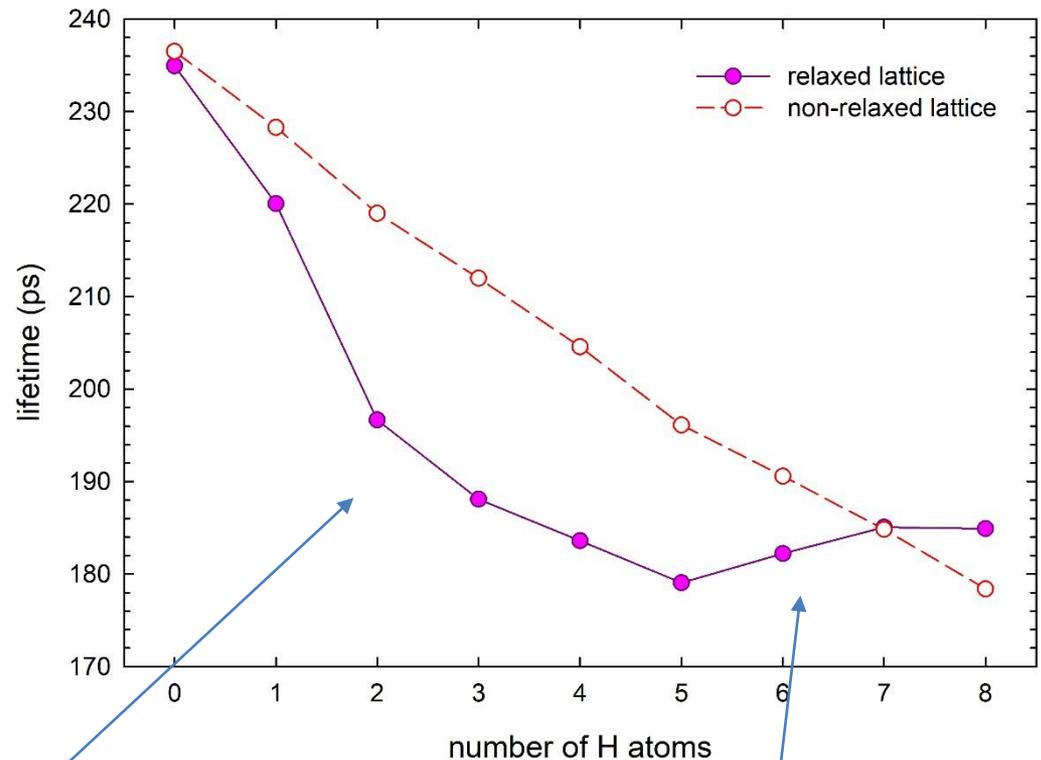
→ linear decrease of lifetime

relaxed lattice

(lowest energy configuration)

→ inward relaxation ($n \leq 5$)

→ outward relaxation ($n > 6$)



inward lattice relaxation

outward lattice relaxation

Hydrogen-charged Ti samples

Ti sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)
annealed in vacuum (1000°C / 2 h)	144.6(6)	100	-	-	-	-
electrochemically charged (20°C / 20 mA / 240 h)	96(6)	18(1)	170(3)	79(2)	350(20)	3(2)
H ₂ gas loaded (150°C / 103 bar / 100 h)	73(88)	10(1)	171(2)	88(1)	400(60)	2(1)

free positrons



dislocations
v+nH complexes



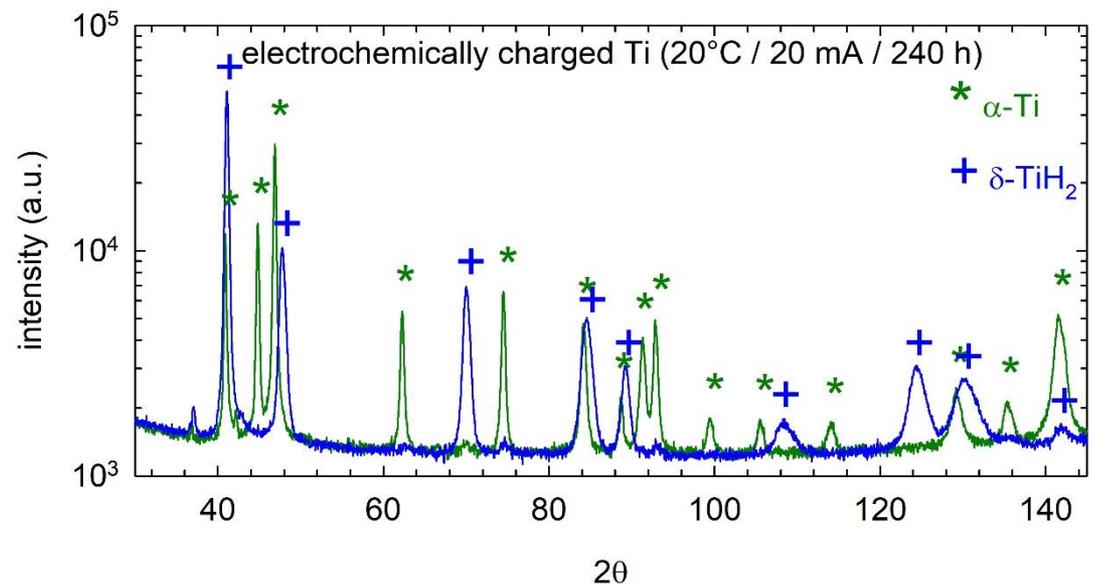
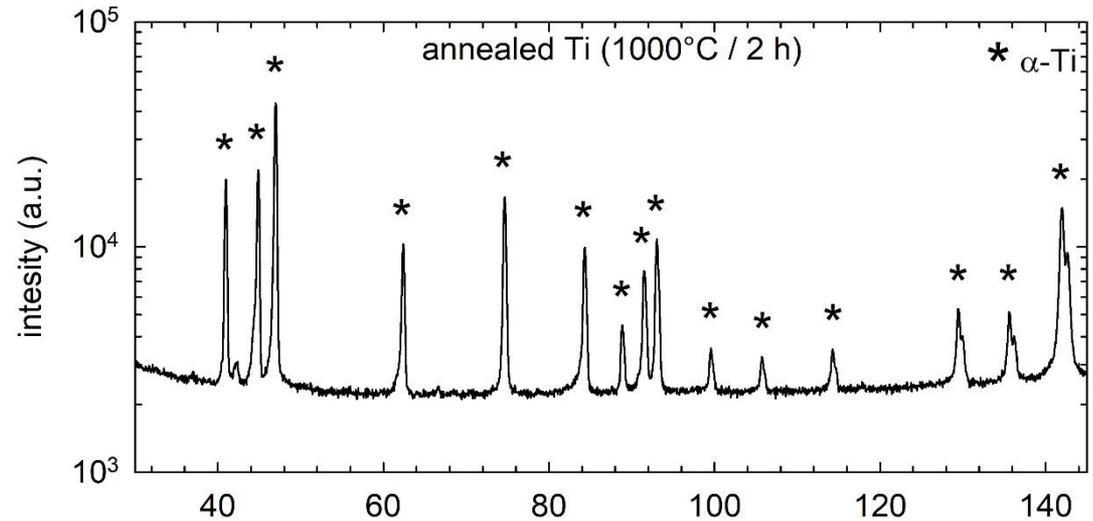
vacancy clusters



XRD phase analysis

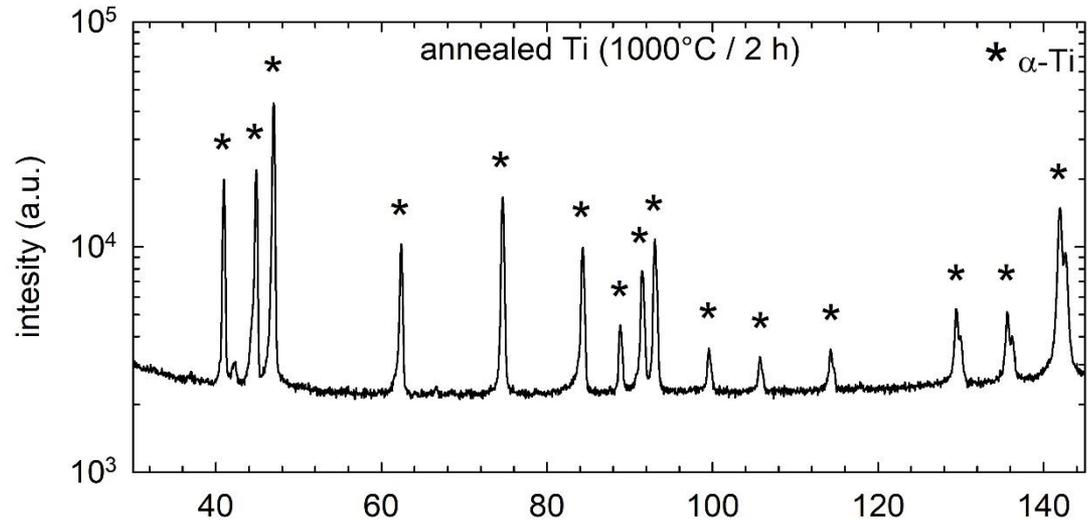
annealed Ti
 → single phase α -Ti

electrochemically charged Ti
 → loaded side: δ -TiH_x phase
 → opposite side: α -Ti phase

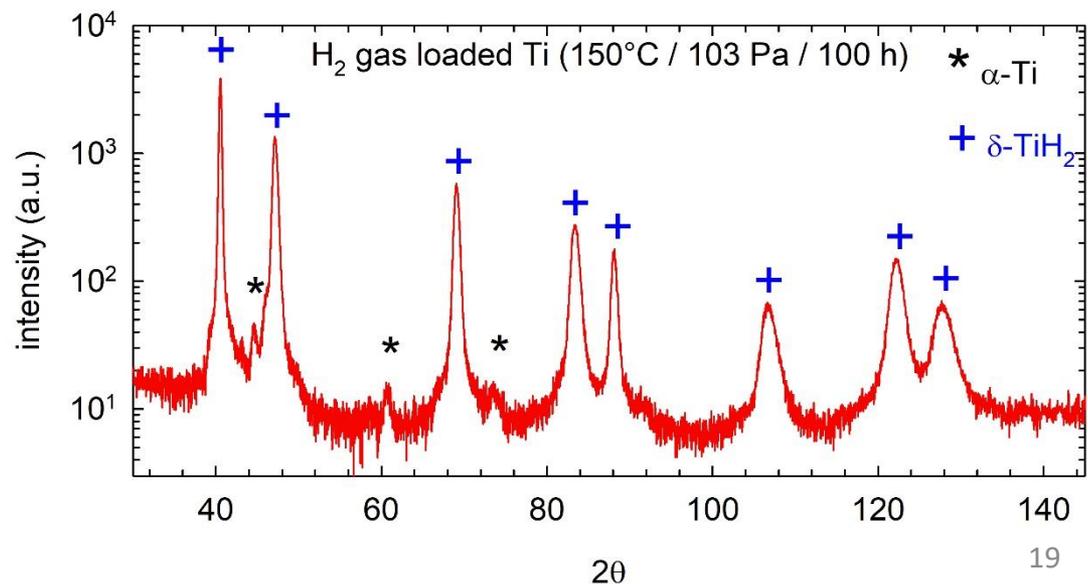


XRD phase analysis

annealed Ti
→ single phase α -Ti



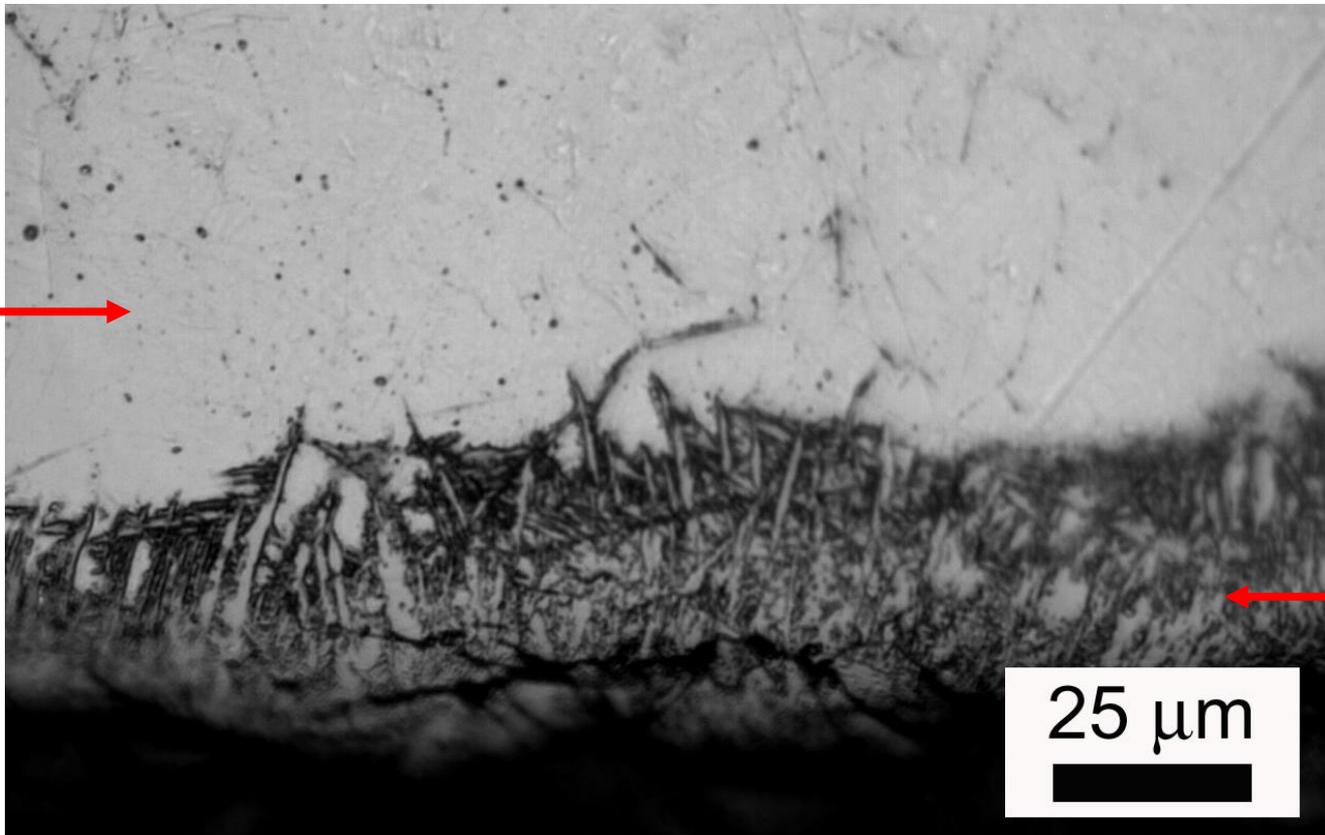
H_2 gas loaded Ti
→ δ -TiH_x phase dominant



α -Ti → δ -TiH_x transformation
leads to plastic deformation and
introduces **dislocations** into the
sample.

δ -hydride formation

sub-surface region transformed into δ -TiH₂
inner region remains in α -Ti



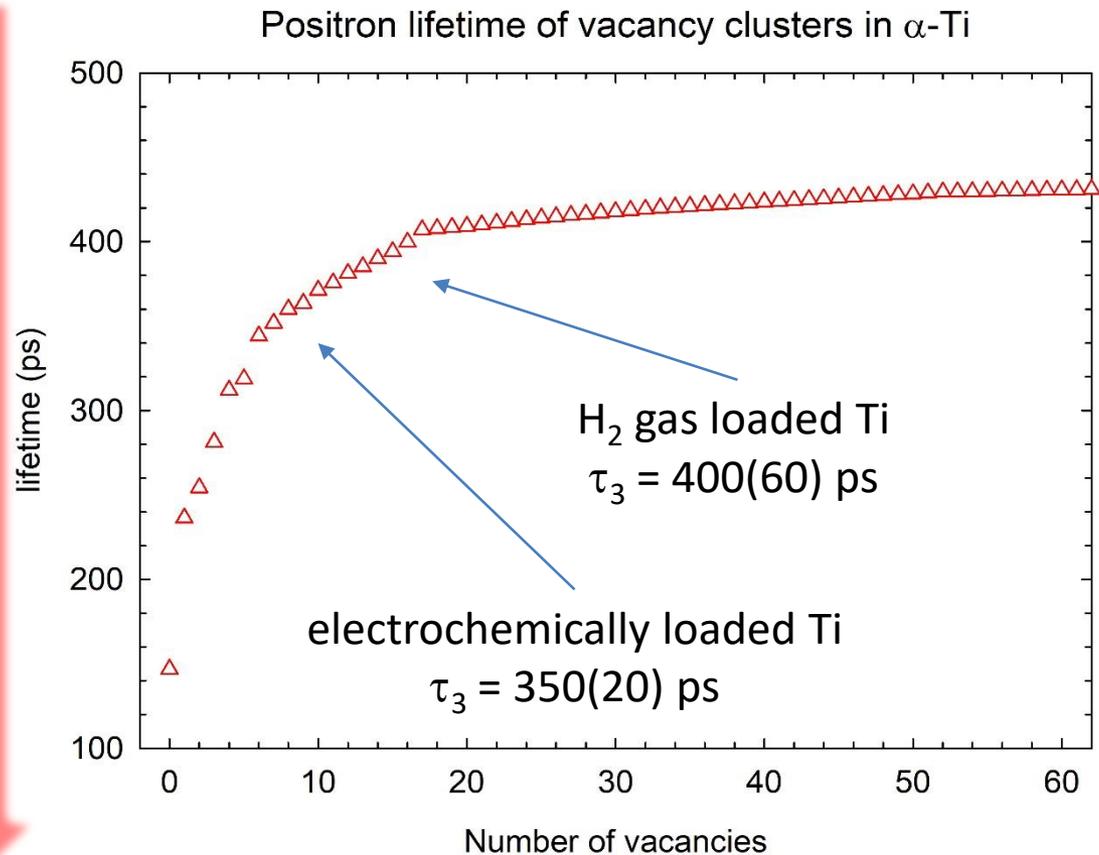
optical micrograph of the cross section of H₂ gas loaded Ti

Vacancy clusters

H-induced vacancies agglomerate into vacancy clusters.

Vacancy clusters are likely decorated with H atoms.

We can estimate the minimal size of vacancy clusters from the calculated lifetimes of “empty” clusters.



electrochemically charged Ti

→ $n > 7$ vacancies

H₂ gas loaded Ti

→ $n > 16$ vacancies

Summary

1. DFT *ab-initio* theoretical modeling of vacancy-hydrogen complexes in α -Ti was performed.
2. Hydrogen atoms significantly reduce vacancy formation energy.
3. Vacancies in Ti are capable of trapping up to 7 H atoms occupying tetrahedral sites.
4. The lifetime of positrons trapped in $v+nH$ complexes with up to 5 H atoms decreases with increasing number of H.
5. For 6 and more H atoms the lifetime increases again due to the outward relaxation caused by repulsive H-H interaction.

Summary

6. Experimental study revealed that H-loading introduced dislocations created by $\alpha\text{-Ti} \rightarrow \delta\text{-TiH}_x$ phase transformation.
7. $\delta\text{-TiH}_x$ phase formation is energetically more favorable than formation of enhanced concentration of $v+n\text{H}$ complexes in $\alpha\text{-Ti}$ matrix.
8. H-induced vacancies diffuse and agglomerate into vacancy clusters capable of trapping H.