Ab initio study of hydrogen behavior in titanium beryllides

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An interest in titanium beryllides as candidate materials for advanced neutron multiplier for the Helium Cooled Pebble Bed breeding blanket of European DEMO fusion reactor is related to their lower tritium retention, lower swelling and higher oxidation resistance in comparison with pure beryllium. The latter was initially suggested as neutron multiplier in the International Thermonuclear Experimental Reactor (ITER) and for the above reasons has a number of limitations compared to beryllides.

One of the most important questions is how much weaker tritium, which is formed as a result of the interaction of high-energy neutrons with the pebbles is bound in titanium beryllides in contrast to pure beryllium. Such an interaction awakes formation of helium bubbles and degradation of the material properties. One of the main promising methods for studying the behavior of hydrogen in titanium beryllides is first-principles modeling technique based on density functional theory.

The present work is devoted to *ab initio* study of hydrogen (isotope effects were neglected and hydrogen was considered instead of tritium) behavior in three titanium beryllides (Be_2Ti, $Be_{17}Ti_2$, $Be_{12}Ti$). All of them have different crystal structure and contain a different number of crystallographically non-equivalent interstitial hydrogen sites.

Both the hydrogen solution energy in defect-free lattice and binding energy with a vacancy are important characteristics in terms of tritium dissolution, retention and release. Static *ab initio* calculations demonstrate that hydrogen solution energy in all interstitial non-equivalent sites is noticeably lower as compared with pure beryllium suggesting an easier dissolution of hydrogen atoms in titanium beryllides. Computation of binding energy of single hydrogen atom with all non-equivalent monovacancies reveals that hydrogen might be trapped by a vacancy without being inside it. The obtained results sheds light on the understanding of earlier tritium release in different titanium beryllides during thermo-desorption experiments and expand our knowledge of their properties.

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SPECIAL JOINT EVENT

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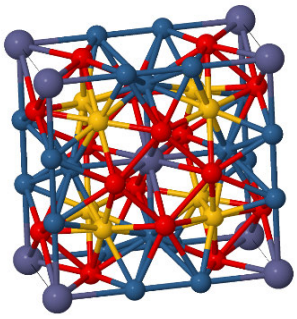
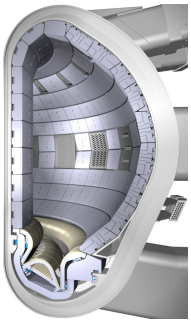
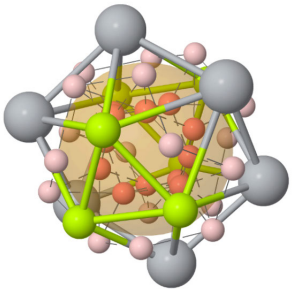
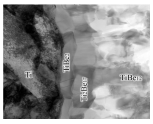




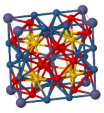


Outline

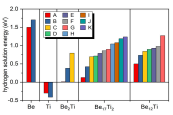
Karlsruhe Institute of Technology



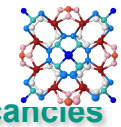
1. Motivation and goals
2. Computational methodology
3. Structure and lattice parameters

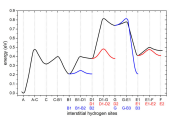


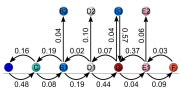
4. Hydrogen in interstitial positions



5. Diffusion of hydrogen in $Be_{12}Ti$





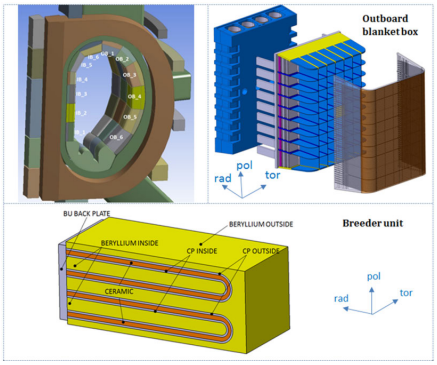


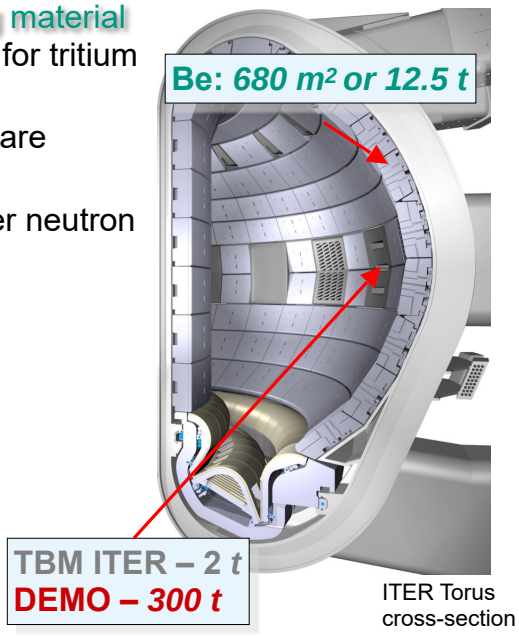
6. Hydrogen in vacancies

7. Conclusions

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)
- Hydrogen isotopes and impurities are implanted into Be first wall tiles
- He and T are produced in Be under neutron irradiation



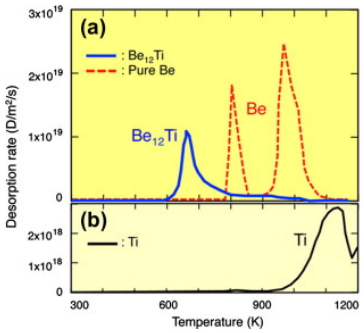


ITER Torus cross-section

K. Ioki et al. Nucl.Fusion **41**(3) 2001 265-275

Motivation and goals

- **Motivation:** Intermetallic beryllium compounds as $Be_{12}Ti$, $Be_{12}V$ and $Be_{12}Zr$ are considered as possible candidates for fusion applications, namely as neutron multiplier for the DEMO breeder blanket to be used instead of pure beryllium.
- **Global Goal:** Elucidation of the origin of the superior properties of beryllides affecting the hydrogen release at lower temperatures by performing comparison of its properties with pure Be.
- **Goal:** elucidation of the origin of the superior properties of titanium beryllides (Be_2Ti, $Be_{17}Ti_2$, $Be_{12}Ti$) and its effect on the hydrogen isotope retention rate
- **Approach:** Ab initio methods



M. Nakamichi et al. JNM 442, 1-3, S465-S471 (2013)

Why do we choose titanium beryllides?

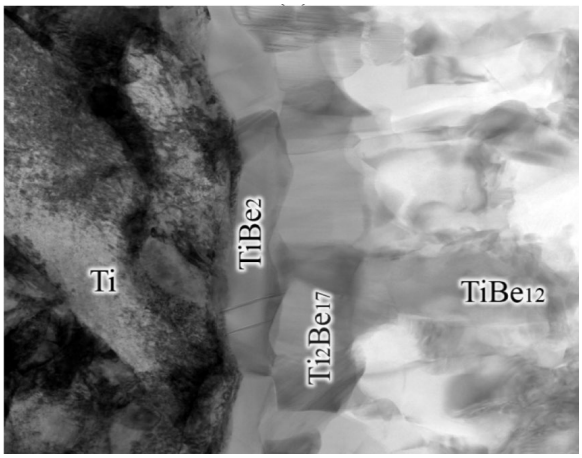
Beryllium vs. **Titanium beryllides**

- ❑ high neutron multiplication efficiency
- ❑ lower melting point
- ❑ lack of oxidation resistance
- ❑ higher tritium retention
- ❑ higher swelling
- ❑ bad compatibility with the structural material

- ❑ lower neutron multiplication efficiency
- ❑ higher melting point
- ❑ higher oxidation resistance
- ❑ lower tritium retention
- ❑ lower swelling
- ❑ good compatibility with the structural materials

Why do we choose titanium beryllides?

Microstructure of Be-Ti composite after extrusion and hot isostatic pressing at 900°C



The structure along with the main phase of $Be_{12}Ti$ contains inclusions of other phases: Be_2Ti, $Be_{17}Ti_2$, pure Ti and Be

- ❑ **Be_2Ti in the form of a thin layer surrounding the pure Ti phase;**
- ❑ **$Be_{17}Ti_2$ in the form of small particles located at the prior Ti phase locations;**
- ❑ **pure Ti and Be phases, which do not dissolve completely**

R.G. Gaisin, V. Chakin, M. Duerrschnabel et al. Nucl Mater Energy 24 (2020) 100771.

Computational methodology

- Static ab-initio calculations (using VASP)
- Projector augmented wave potential (PAW)
- Generalized gradient approximation (GGA)
- Fermi broadening: 0.2 eV
- Cut-off energy: 487 eV
- No volume and shape relaxation
- No restrictions on relaxation of atoms

Hydrogen solution energy

$$E_s = E_{total}^{\mathrm{Be+H}} - E_{total}^{\mathrm{Be}} - E_{ref}^{\mathrm{H}}$$

$E_{total}^{\mathrm{Be+H}}$ and E_{total}^{Be} are the total energies of the simulation cells with and without hydrogen

$E_{ref}^{\mathrm{H}} = -3.3590\ \mathrm{eV}$ is the energy of hydrogen atom in H_2 molecule

Hydrogen binding energy

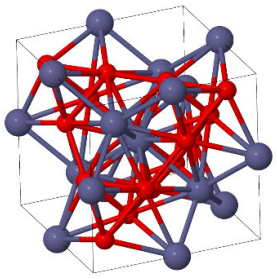
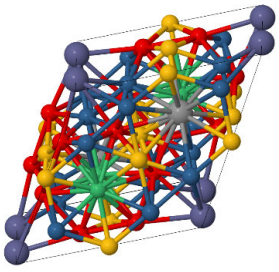
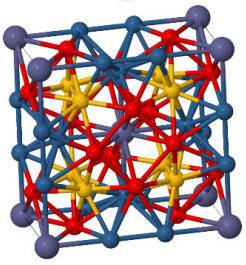
$$E_b = E(H+V) - E(V) + E(H_I) - E_{bulk}$$

$E(H+V)$ and $E(V)$ are the total energies of the simulation cells with vacancy and one hydrogen atom and only with a vacancy

$E(H_I)$ is the energy of hydrogen atom in interstitial position

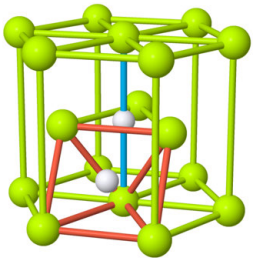
E_{bulk} is the energy of the bulk

Structure and lattice parameters

	Be_2Ti cubic	$Be_{17}Ti_2$ hexagonal	$Be_{12}Ti$ tetragonal
			
Lattice parameters	a = 4.539 Å	a = 7.333 Å c = 7.164 Å	a = 7.234 Å c = 4.151 Å
Computational cell	32 Be atoms 16 Ti atoms	34 Be atoms 4 Ti atoms	48 Be atoms 4 Ti atoms
Cryst. non-eq. atomic sites	**2** (1Be+1Ti)	**6** (4Be+2Ti)	**4** (3Be+1Ti)

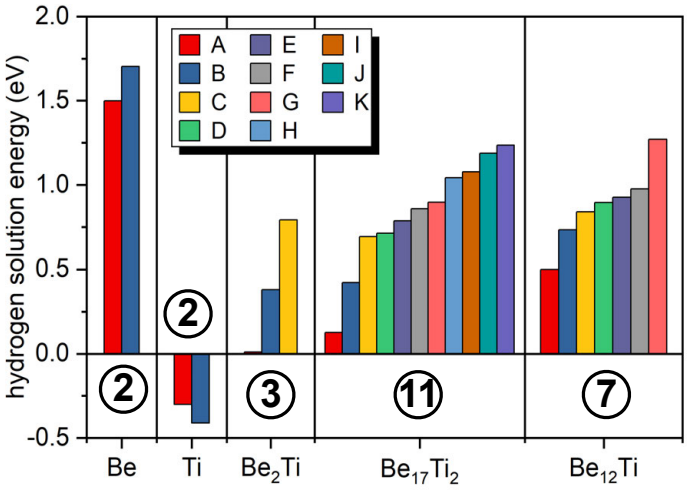
Hydrogen in interstitial positions

Be
hexagonal



- Octahedral (O)
- Basal Tetrahedral (BT)

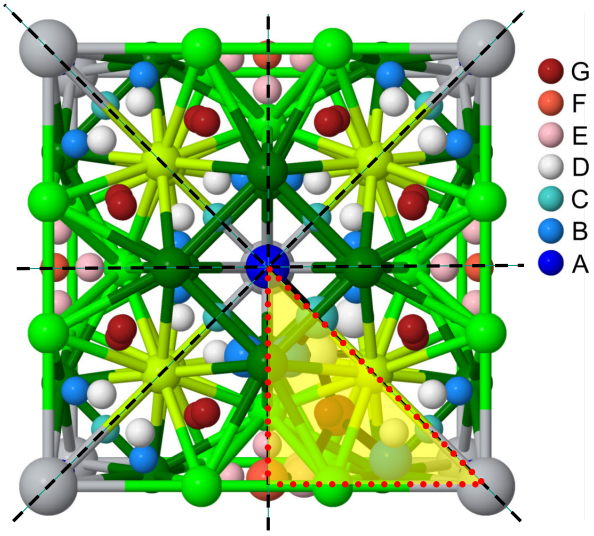
Hydrogen was placed in the center of all possible non-equivalent tetrahedra

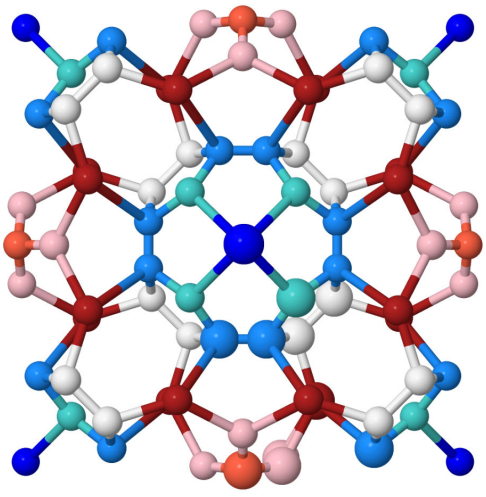


Positive solution energy (endothermic)
Negative solution energy (exothermic)

Easier dissolution of hydrogen atoms in the beryllides

Diffusion in $Be_{12}Ti$





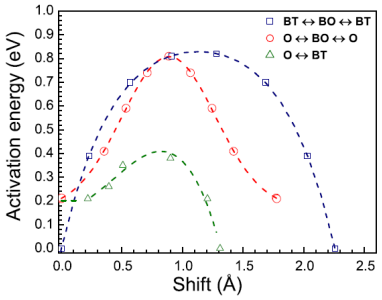
7 energetically nonequivalent hydrogen interstitial sites (A-G) within $Be_{12}Ti$ lattice

Hydrogen path through non-equivalent interstitial sites and 10 jumps between them

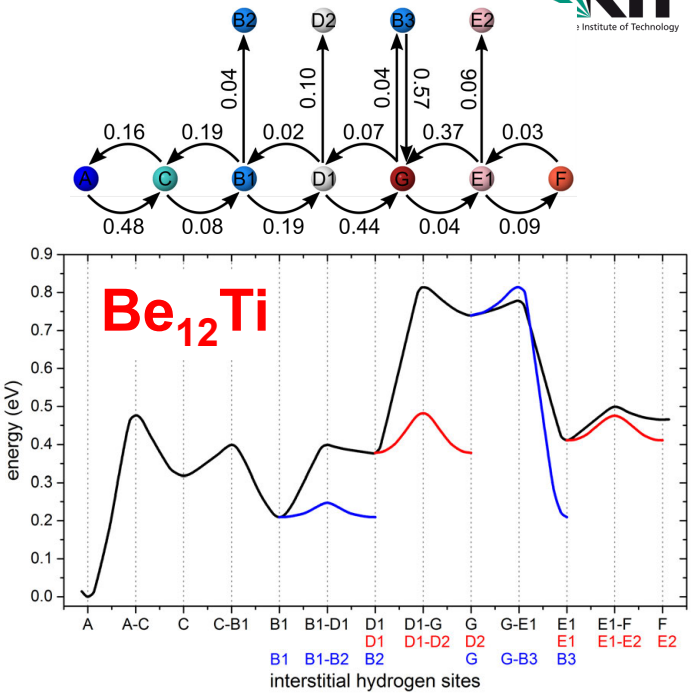
D.V. Bachurin, C. Stihl, P.V. Vladimirov, Comp. Mat. Sci. 187 (2021) 109921.

Diffusion in Be and $Be_{12}Ti$

Be

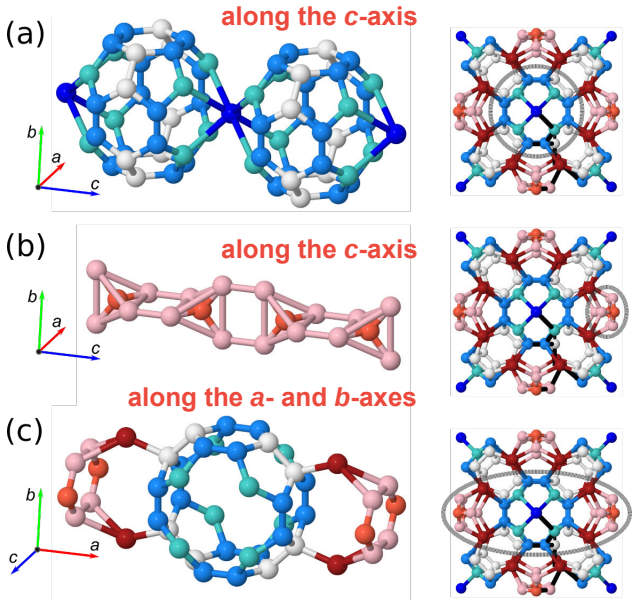


M.G. Ganchenkova, P.V. Vladimirov, V.A. Borodin, J Nucl Mater 386-88 (2009) 79-81.

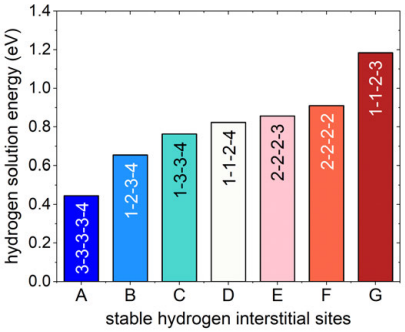


D.V. Bachurin, C. Stihl, P.V. Vladimirov, Comp. Mat. Sci. 187 (2021) 109921.

Diffusion in $Be_{12}Ti$

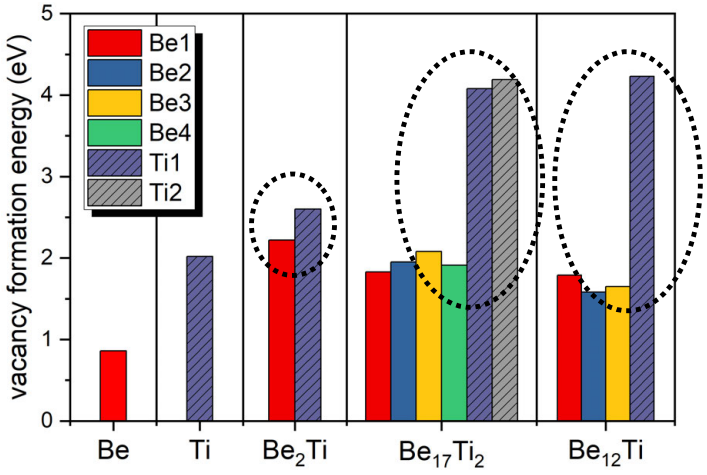


7 energetically nonequivalent H interstitial sites (A-G) within $Be_{12}Ti$ lattice



D.V. Bachurin, C. Stihl, P.V. Vladimirov, Comp. Mat. Sci. 187 (2021) 109921.

Vacancy formation energy



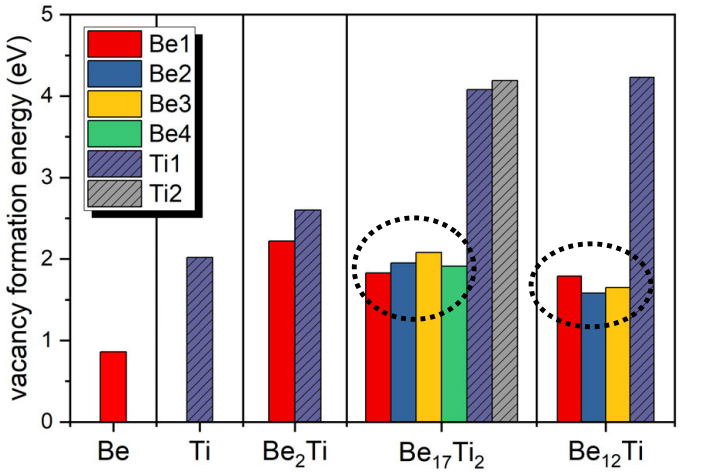
$$E_f^V = E_{n-1}^V - E_n + E_{coh}^{Be,Ti}$$

E_{n-1}^V and E_n are the total energies of the simulation cells with and without vacancy

E_{coh}^{Be} = -3.7660 eV
E_{coh}^{Ti} = -7.7627 eV

- The formation energies of Be vacancies in $Be_{12}Ti$ and $Be_{17}Ti_2$ are circa two times less then those of Ti vacancies (except for Be_2Ti)

Vacancy formation energy



$$E_f^V = E_{n-1}^V - E_n + E_{coh}^{Be,Ti}$$

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E_{coh}^{Be} = -3.7660 eV
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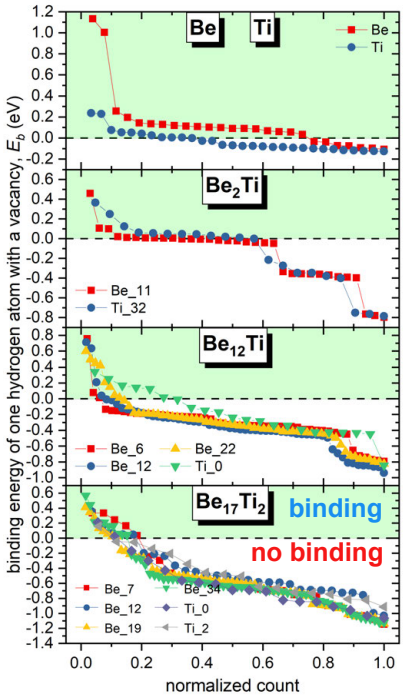
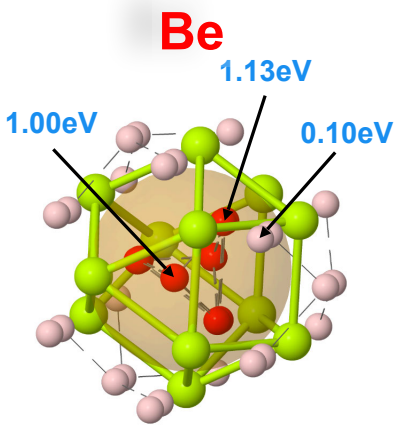
- The formation energies of Be vacancies in $Be_{12}Ti$ and $Be_{17}Ti_2$ are circa two times less than those of Ti vacancies (except for Be_2Ti)
- The formation energies of Be vacancies in $Be_{12}Ti$ and $Be_{17}Ti_2$ are very close to each other

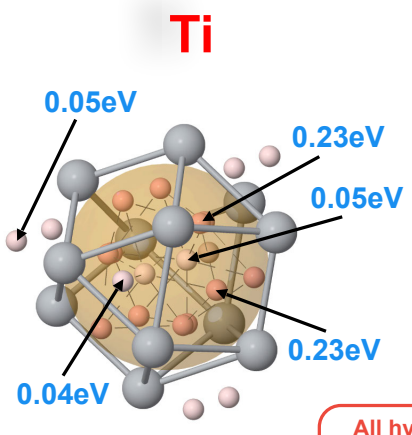
Binding energy of hydrogen atom in vacancy



- Binding energy of H atom in Ti vacancy is circa 0.9 eV lower than that in Be
- (Be_2Ti) Binding energies of H atom with Be and Ti vacancies are 0.36 and 0.46eV, respectively
- ($Be_{12}Ti$) Binding energies of H atom with Be vacancies are 0.76, 0.71 and 0.60eV, with Ti vacancy is 0.34eV
- ($Be_{17}Ti_2$) Binding energies of H atom with Be vacancies are 0.34, 0.36, 0.41 and 0.56eV, with Ti vacancies are 0.21 and 0.16eV
- Binding energy of H atom with Be vacancy is always higher than with Ti vacancy

Binding energy of hydrogen atom in vacancy



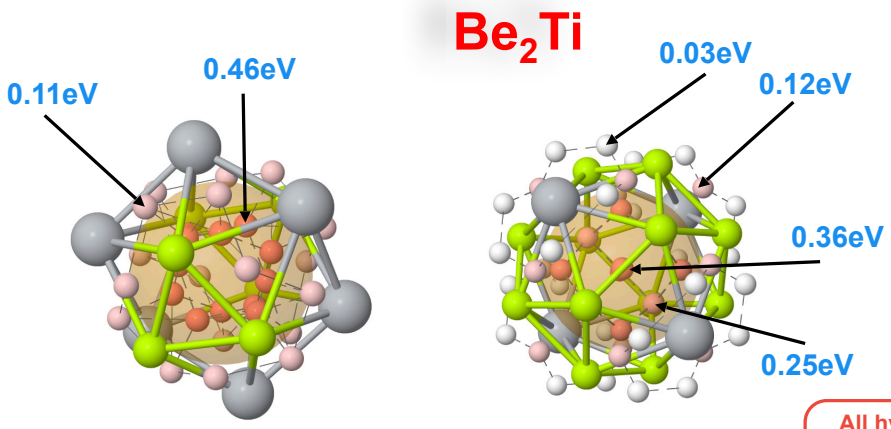


All hydrogen atoms with negative binding energy were made invisible

Binding energy of H atom with Be vacancy is significantly higher than that in Ti

Some hydrogen atoms located outside a vacancy are trapped by it

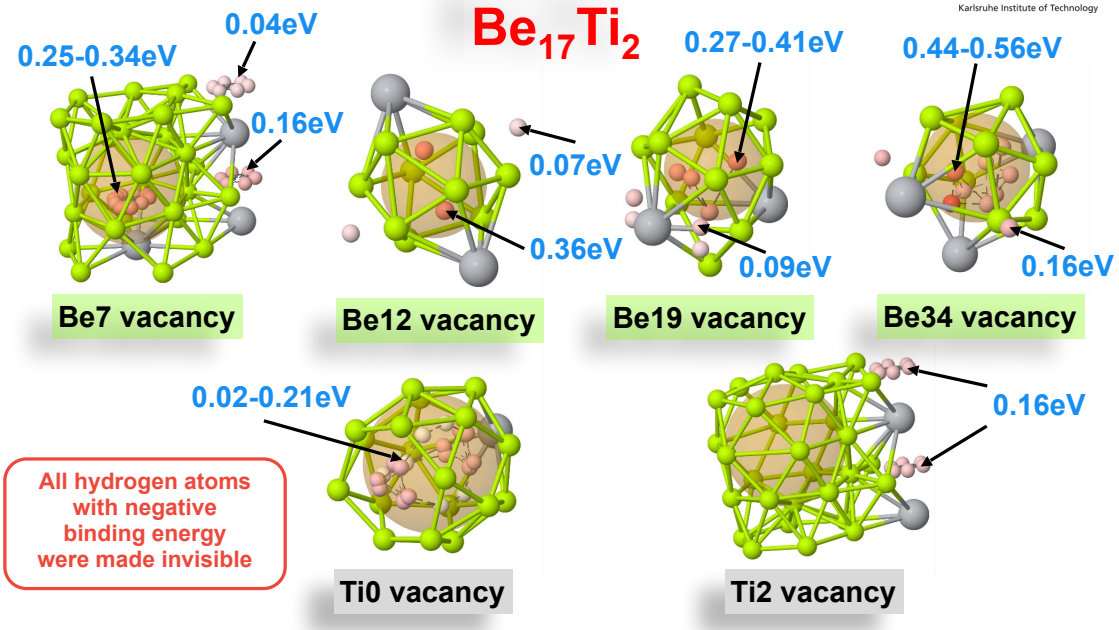
Binding energy of hydrogen atom in vacancy



Binding energy of H atom with vacancy of Be_2Ti is at least circa 0.5 eV lower than that in pure Be

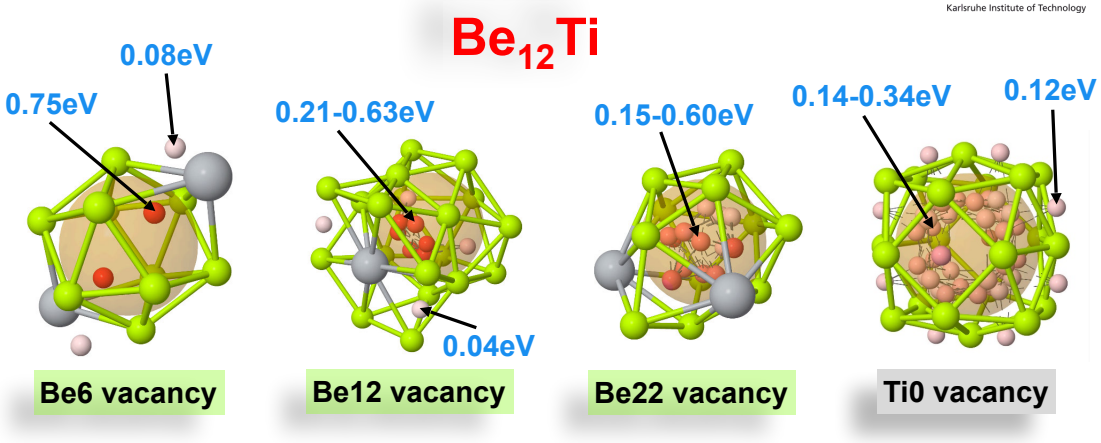
Some hydrogen atoms located outside a vacancy are trapped by it

Binding energy of hydrogen atom in vacancy



Binding energy of H atom in a vacancy of $Be_{17}Ti_2$ is at least 0.4 eV lower than that in pure Be

Binding energy of hydrogen atom in vacancy



Binding energy of H atom in a vacancy of $Be_{12}Ti$ is at least 0.4 eV lower than that in pure Be

Binding energy of H atom inside the vacancies of titanium beryllides is always lower then outside them and is in the range of 0.04-0.16 eV

Conclusions

- Hydrogen solution energy in interstitial positions of titanium beryllides are at least 0.2-0.7 eV lower then that for Be suggesting easier dissolution of hydrogen atoms in the studied beryllides.
- In titanium beryllides hydrogen atoms prefer to occupy the interstitial sites near Ti.
- Formation energy of Be vacancies is circa two times less than the corresponding energy for Ti vacancies in $Be_{12}Ti$ and $Be_{17}Ti_2$. In Be_2Ti the formation energies of Be and Ti vacancies does not differ much from each other.
- Some hydrogen atoms might be trapped by a vacancy without being inside it.
- Hydrogen binding with a monovacancy is 0.4-0.5 eV lower in the studied titanium beryllides, suggesting easier release of hydrogen from beryllides as compared to pure Be.
- The latter conclusion is consistent with the experimental data on deuterium release from Be and $Be_{12}Ti$ after deuterium implantation.