## Effect of impurities on microstructural evolution under irradiation in beryllium

P.V. Vladimirov[1], D.V. Bachurin[1], C. Stihl[1] and N. Zimber[1]

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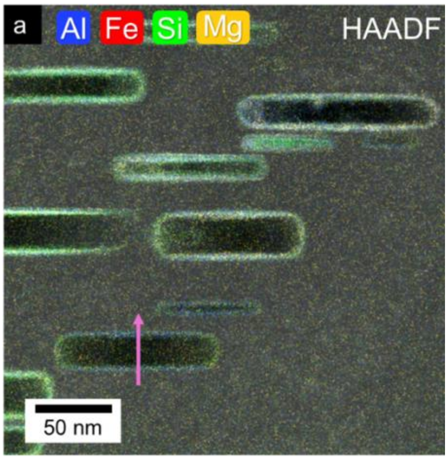
*76344 Eggenstein-Leopoldshafen, Germany*

Impurities are known to affect mechanical properties of beryllium, but their effect on development of irradiation induced microstructure is still unknown. In this contribution we are making further attempt to reveal behavior of impurities in neutron irradiated beryllium pebbles by using both analytical transmission electron microscope (TEM) and first principles computer simulations.

TEM studies have revealed Al-Fe-Be precipitates, complex multiple phase precipitates, homogeneous segregations of elements to grain boundaries as well as abundant precipitation along dislocations. All precipitates are richly decorated with helium bubbles which are smaller in size than typical bubbles inside grains. Precipitate-free and helium-bubble-free zones were observed along grain boundaries.




Using density functional theory approach, we have calculated interaction of typical solutes found in beryllium, namely, Al, Fe, Cr, Mg and Si with vacancies, interstitials and free surfaces which can simulate a surface of helium bubbles. Interesting correlation has been revealed: an impurity which has attractive binding with a vacancy has also positive affinity to free surface. In particular, Al, Mg and Si are strongly bound with vacancies and also attracted by the free surfaces. This result is supported by the EDX measurements, (see Fig. above) which reveal decoration of He bubbles with Al, Si and Mg, while Fe is homogeneously distributed. Those impurities which repulse vacancies are attracted by self-interstitials, however, no correlation with the formation volume of respective substitutional atoms was found in this case.

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KIT – The Research University in the Helmholtz Association **www.kit.edu**

## Outline

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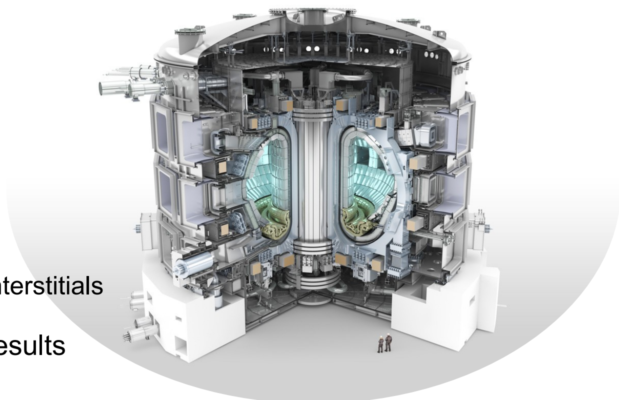
- Introduction
  - Beryllium as neutron multiplier
  - Typical impurities in Be
  - Behavior under irradiation
- Calculation methods
- Results
  - DFT results
    - Solutes and their dipole tensors
    - Interaction with vacancies and interstitials
    - Interaction with surfaces
  - Comparison with experimental results
- Discussion/Conclusions



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## Beryllium as neutron multiplier in ITER TBM

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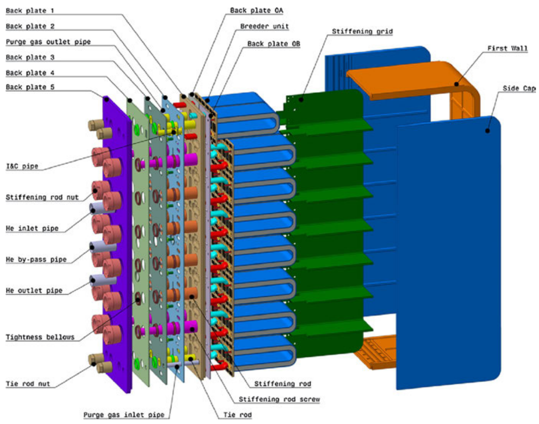
- Lithium and beryllium are needed to increase TBR and close fuel cycle
- Beryllium will be used as 1-mm pebbles filling space within BU around Li-ceramic layers




M. Zmitko, et al. *Development and qualification of functional materials for the European HCPB TBM*, https://doi.org/10.1016/j.fusengdes.2018.05.014

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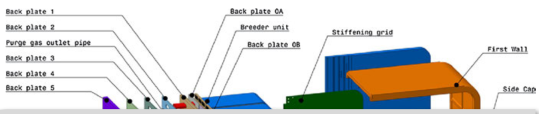
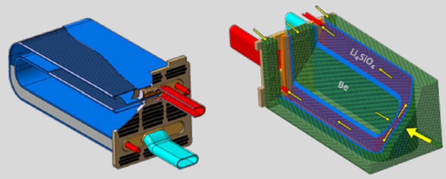
## Beryllium as neutron multiplier in ITER TBM

Karlsruhe Institute of Technology

- Lithium and beryllium are needed to increase TBR and close fuel cycle
- Beryllium will be used as 1-mm pebbles filling space within BU around Li-ceramic layers
- Formation of gas filled bubbles (swelling) is critical for tritium accumulation



BU = Breeder Unit
Consists of Li-cermics and Be interchanging pebble beds

M. Zmitko, et al. *Development and qualification of functional materials for the European HCPB TBM*, https://doi.org/10.1016/j.fusengdes.2018.05.014

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## Impurities in Be

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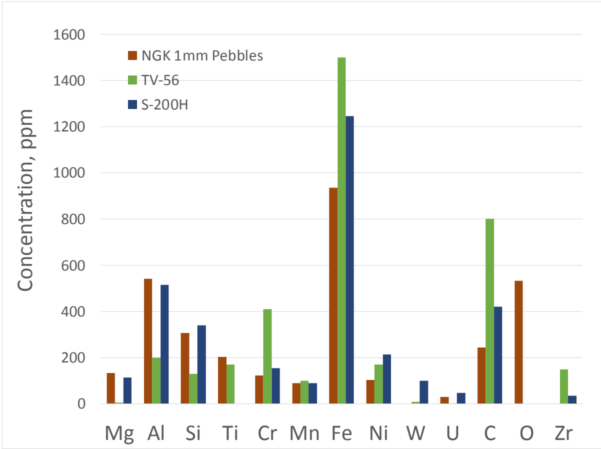
- Why impurities are important:
  - Mechancial properties (hot shortness)
  - Activation under irradiation (e.g., U)
  - Affect microstructure development under irradiation
- Major metallic impurities are
  - Mg, Al, Si,
  - Cr, Fe
- Major non-metals:
  - C, O
- Impurities produced by neutron-induced nuclear transmutations:
  - He, Li

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## Impurities in as received Be

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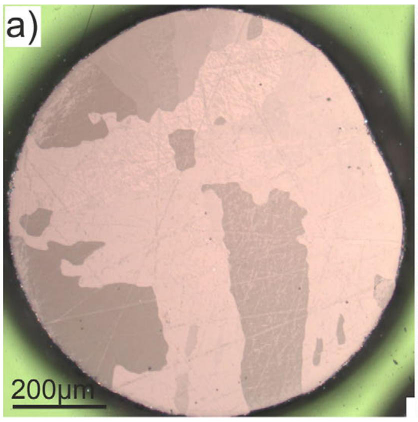


N. Zimber PhD Thesis,
10.5445/IR/1000139959

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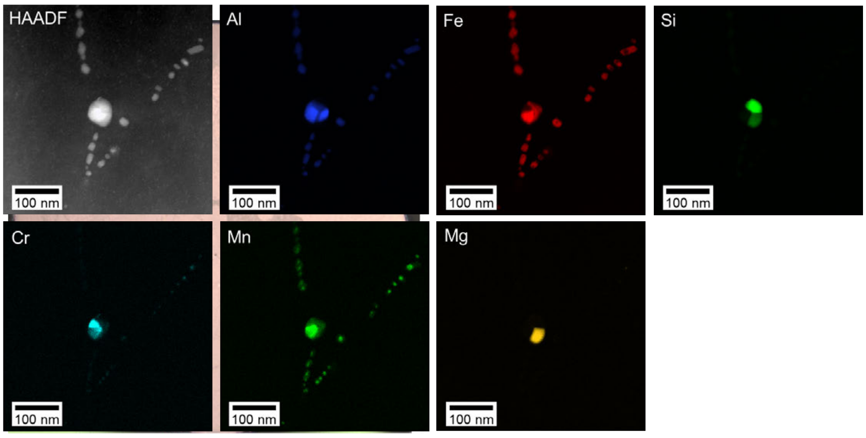
## Impurities in as received Be

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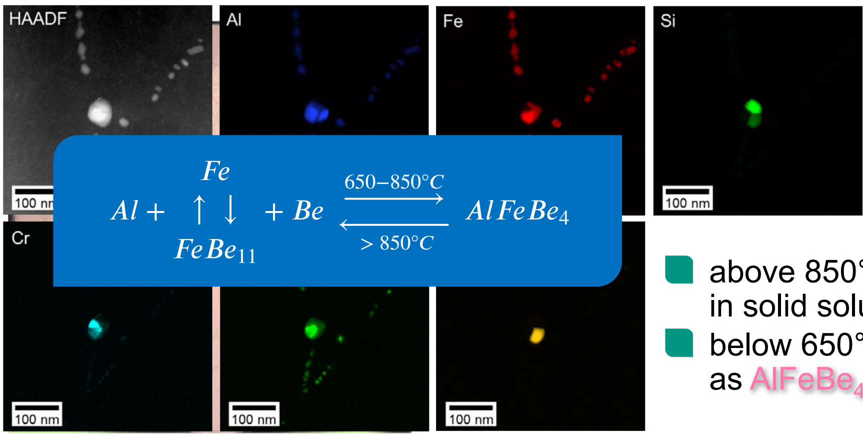


$$Al + \underset{FeBe_{11}}{\overset{Fe}{\uparrow\downarrow}} + Be \underset{>850°C}{\overset{650-850°C}{\rightleftarrows}} AlFeBe_4$$

- above 850°C Al und Fe in solid solution
- below 650°C precipate as $AlFeBe_4$

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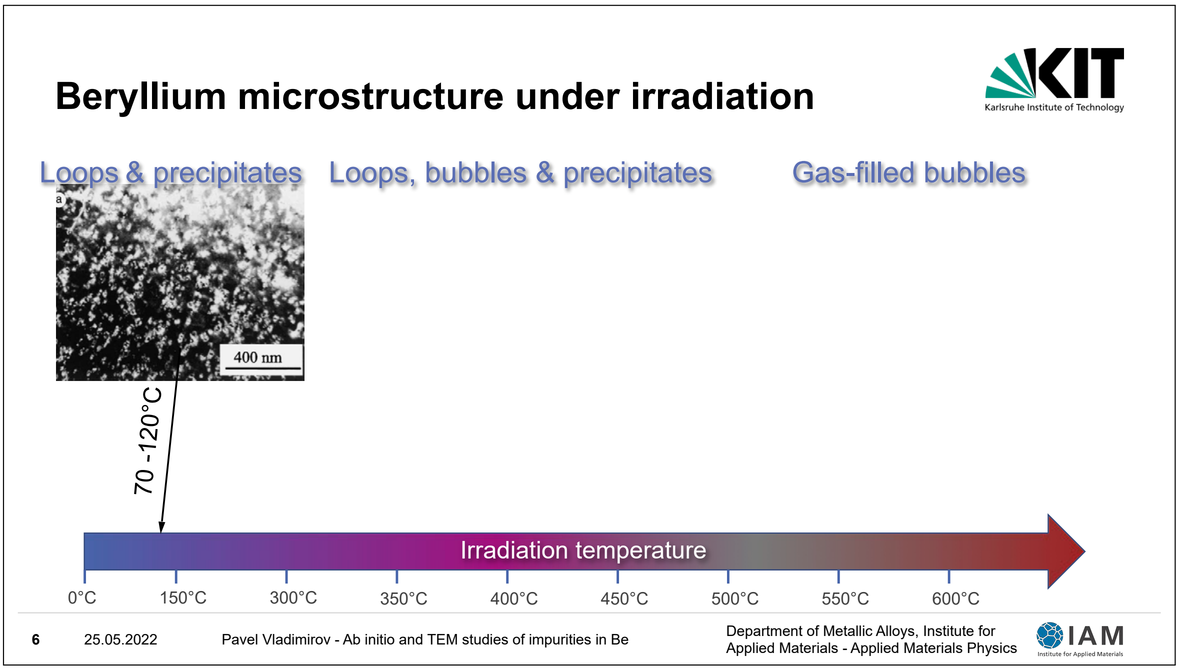
Beryllium microstructure under irradiation
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Loops & precipitates
Loops, bubbles & precipitates
Gas-filled bubbles
400 nm
70 -120°C
Irradiation temperature
0°C
150°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
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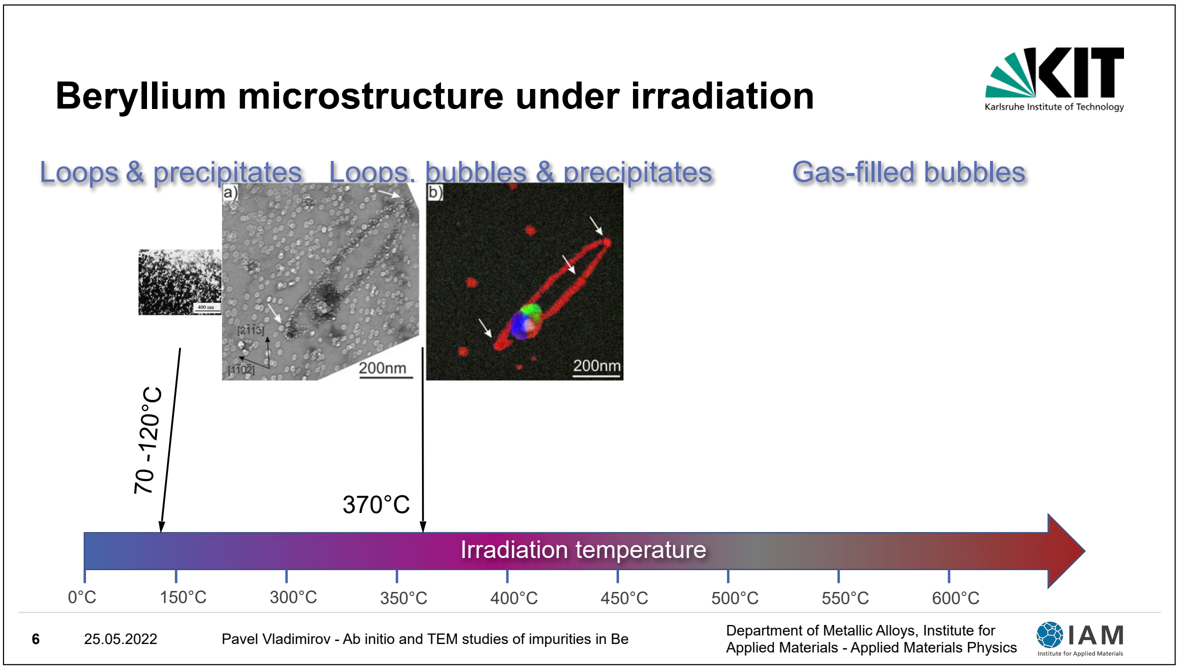
Beryllium microstructure under irradiation
Karlsruhe Institute of Technology
Loops & precipitates
Loops, bubbles & precipitates
Gas-filled bubbles
a)
b)
200nm
200nm
70 -120°C
370°C
Irradiation temperature
0°C
150°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
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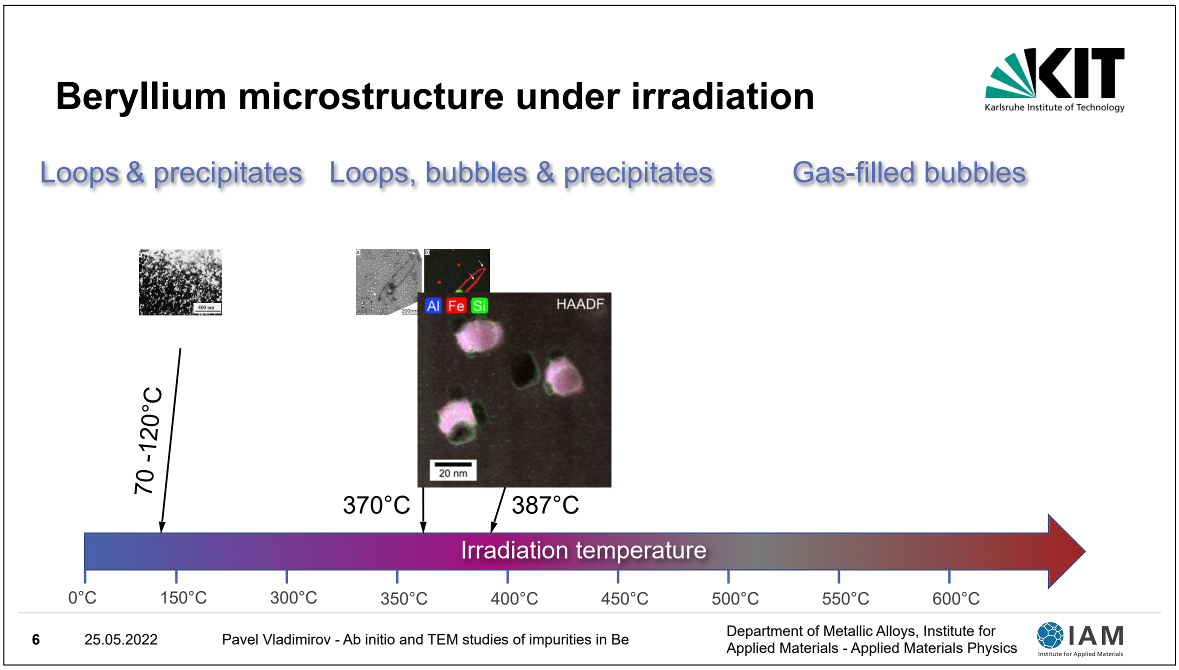
Beryllium microstructure under irradiation
Karlsruhe Institute of Technology
Loops & precipitates
Loops, bubbles & precipitates
Gas-filled bubbles
Al Fe Si
HAADF
20 nm
70 -120°C
370°C
387°C
Irradiation temperature
0°C
150°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
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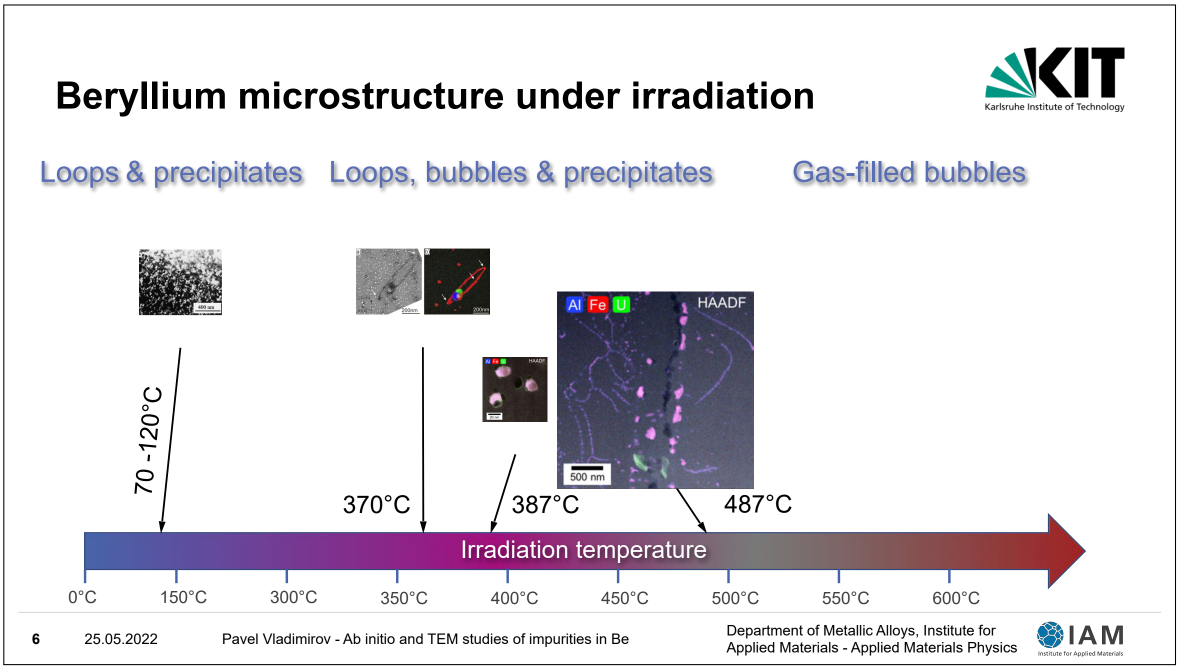
Beryllium microstructure under irradiation
Karlsruhe Institute of Technology
Loops & precipitates
Loops, bubbles & precipitates
Gas-filled bubbles
Al Fe U
HAADF
500 nm
70 -120°C
370°C
387°C
487°C
Irradiation temperature
0°C
150°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
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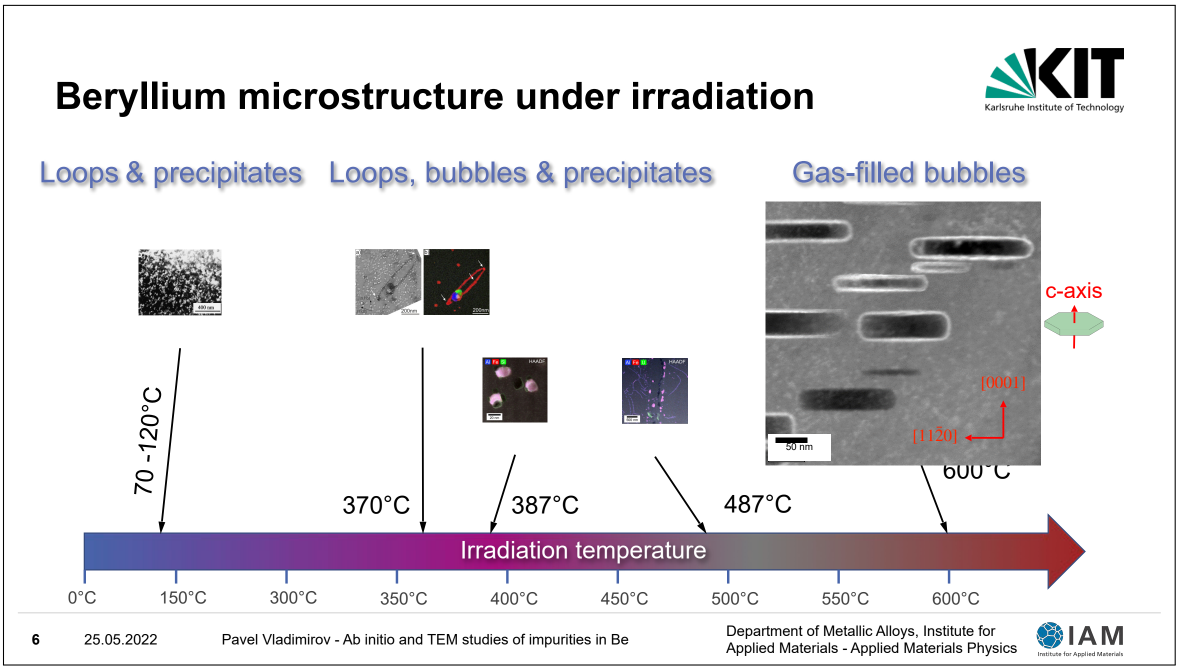
Beryllium microstructure under irradiation
Karlsruhe Institute of Technology
Loops & precipitates
Loops, bubbles & precipitates
Gas-filled bubbles
c-axis
[0001]
50 nm
70 -120°C
370°C
387°C
487°C
600°C
Irradiation temperature
0°C
150°C
300°C
350°C
400°C
450°C
500°C
550°C
600°C
6
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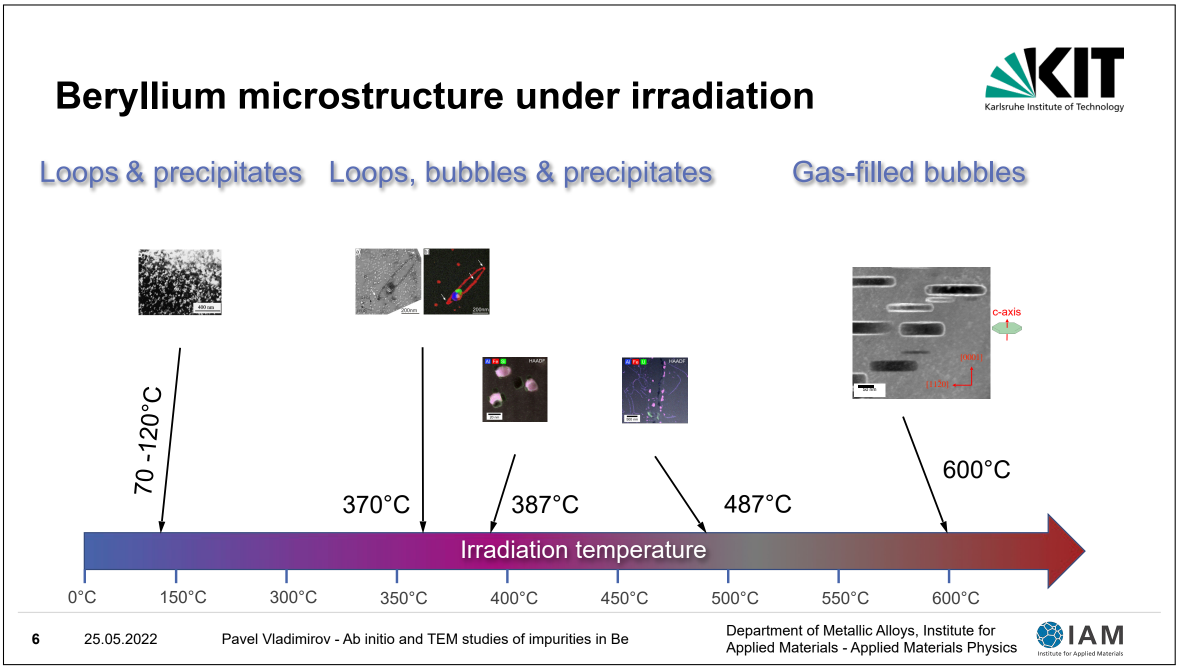
Beryllium microstructure under irradiation
Karlsruhe Institute of Technology
Loops & precipitates
Loops, bubbles & precipitates
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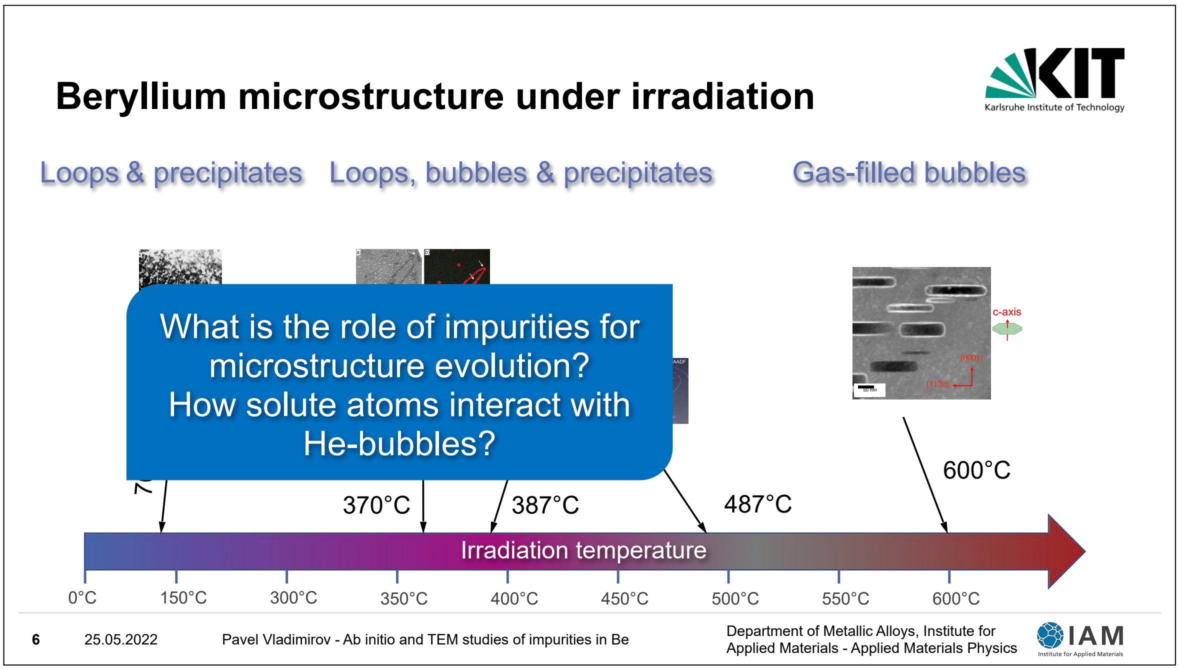


## Simulation methods

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### Density Functional Theory

- VASP 5.3 or 6.2.0
- Generalized Gradient Approximation (GGA)
- Pseudopotentials:
  - Plain Augmented Waves (PAW), xc=PBE_54
  - Li: 2s1 Al: 3s2 3p1
  - Be: 2s2 Si: 3s2 3p2
  - Mg: 3s2 Cr: 4s1 3d5
  - Fe: 3d6 4s2
- Gamma centered Monkhorst-Pack k-point grid
  13 × 13 × 13 or KSPACING = 0.12016
- Energy cutoff ENCUT ≥ 450 eV

- Simulation cell sizes for solute-vacancy interaction:
  - 4 × 4 × 3 – 96 atoms
  - 5 × 5 × 3 – 150 atoms
  - 6 × 6 × 3 – 216 atoms
- Simulation cell sizes for slabs:
  - $(0001)$ 4×4×12 – 384 atoms
  - $(1\bar{1}00)$ 3×4×17 – 168 atoms
- Migration barrier calculations:
  - NEB
  - Dimer

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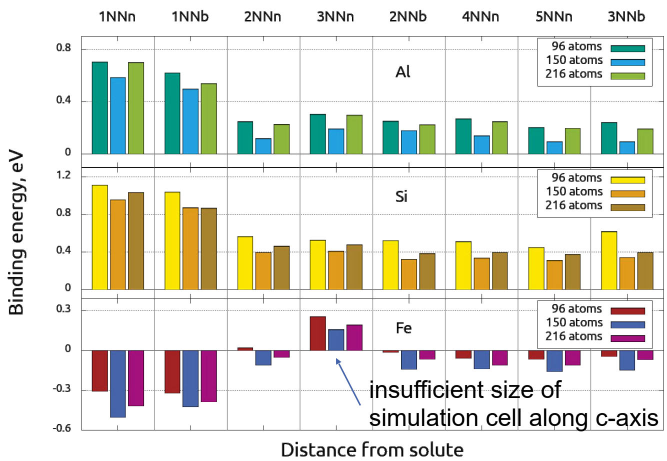
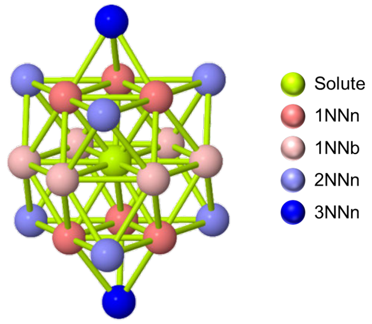
## Solute-vacancy interaction




M. Klimenkov et al., *New insights into microstructure of irradiated beryllium based on experiments and computer simulations*, Sci. Rep. 10 (2020) 8042. https://doi.org/10.1038/s41598-020-64654-5

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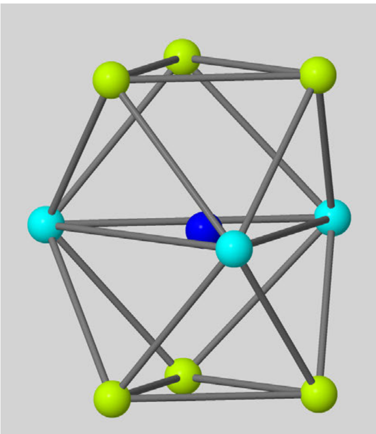
## Interaction of solutes with SIAs in Be


BO configuration of SIA

- Self-interstitial configurtion with the lowest energy (ground state) is basal octahedral (BO) position.
- Interaction with solute atom changes this ground state configuration dramatically in some cases

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## Interaction of solutes with SIAs

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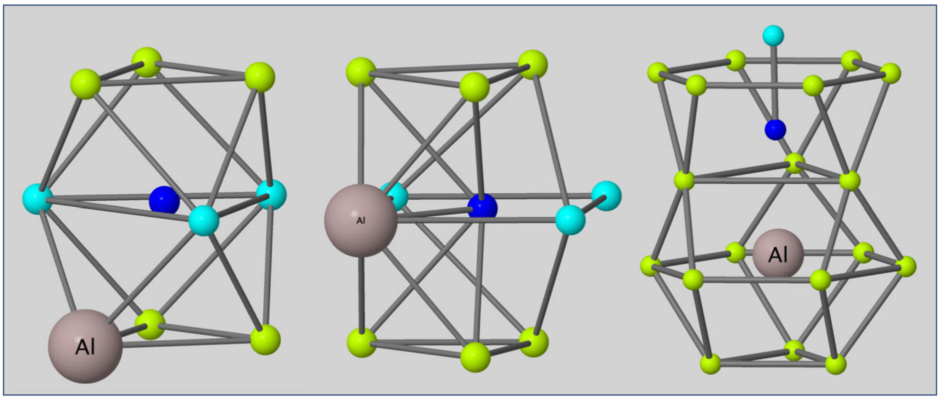


adjacent plane | same basal plane | along c-axis

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## Interaction of solutes with SIAs

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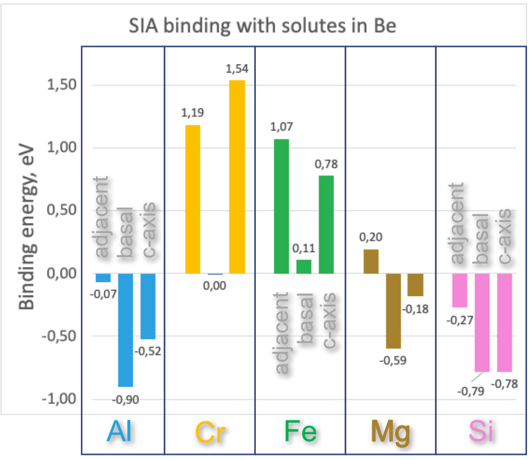


- SIAs are bound to Cr and Fe in non-basal configurations, but are repelled from Al, Mg and Si.
- Largest repulsion and lowest binding are observed for basal configurations.
- For both Cr and Fe, basal configuration is loosely bound => conversion from non-basal to basal configuration might be an important step for SIA detrapping.

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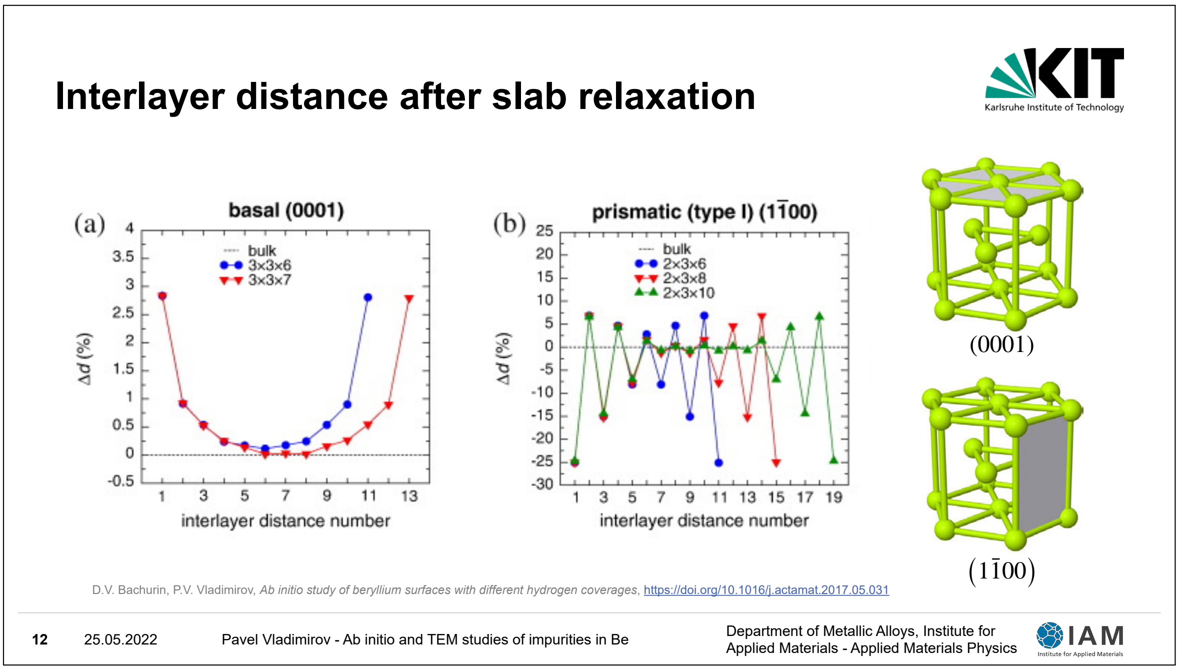
Interlayer distance after slab relaxation
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(a)
basal (0001)
bulk
3x3x6
3x3x7
Δd (%)
interlayer distance number
(b)
prismatic (type I) (1$\bar{1}$00)
bulk
2x3x6
2x3x8
2x3x10
Δd (%)
interlayer distance number
(0001)
(1$\bar{1}$00)
D.V. Bachurin, P.V. Vladimirov, Ab initio study of beryllium surfaces with different hydrogen coverages, https://doi.org/10.1016/j.actamat.2017.05.031
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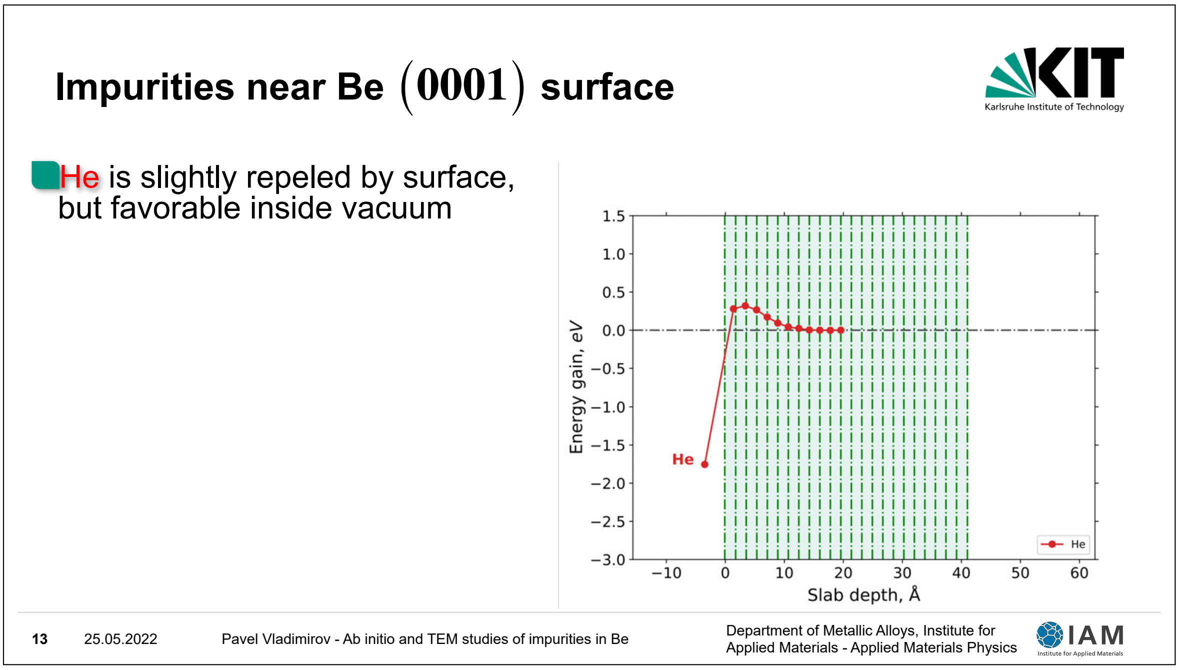
Impurities near Be (0001) surface
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He is slightly repeled by surface, but favorable inside vacuum
Energy gain, eV
Slab depth, Å
He
He
13
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## Impurities near Be (0001) surface

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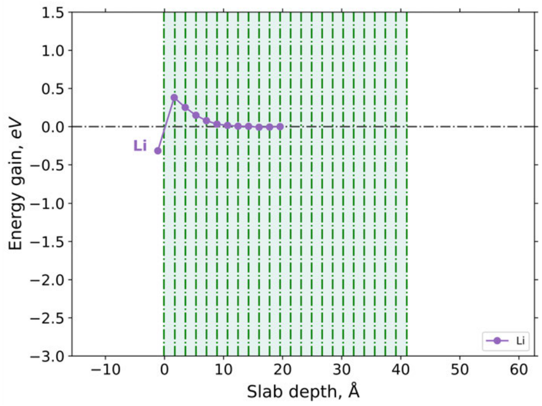
- He is slightly repeled by surface, but favorable inside vacuum
- Li is also slighly repeled, but favorable at the surface

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## Impurities near Be (0001) surface

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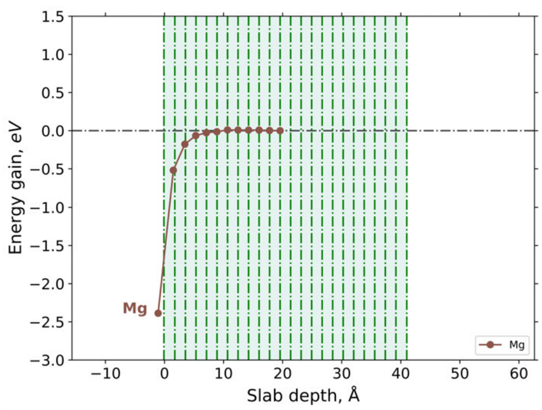
- Li is also slighly repeled, but favorable at the surface
- Mg is attracted by surface

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## Impurities near Be (0001) surface

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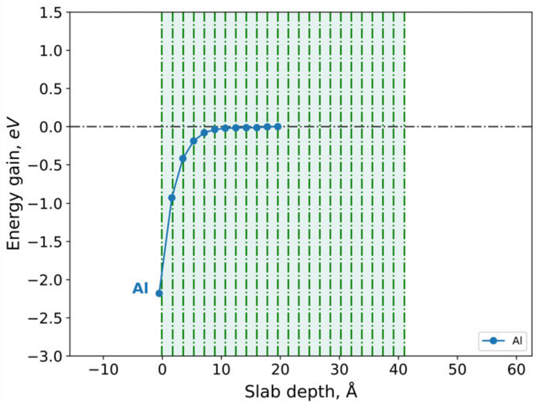
- He is slightly repeled by surface, but favorable inside vacuum
- Li is also slighly repeled, but favorable at the surface
- Mg is attracted by surface
- Al is similar to Mg

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## Impurities near Be (0001) surface

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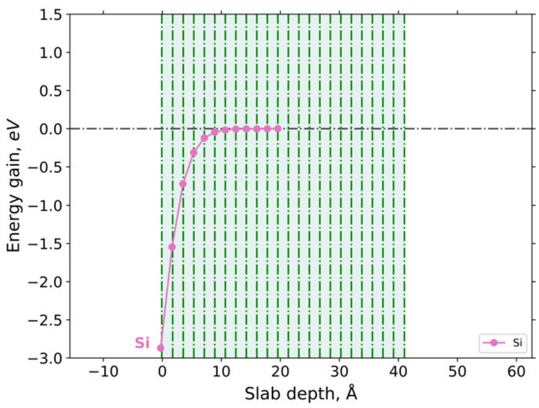
- He is slightly repeled by surface, but favorable inside vacuum
- Li is also slighly repeled, but favorable at the surface
- Mg is attracted by surface
- Al is similar to Mg
- Si is the most favorable impurity at the surface

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## Impurities near Be $(0001)$ surface

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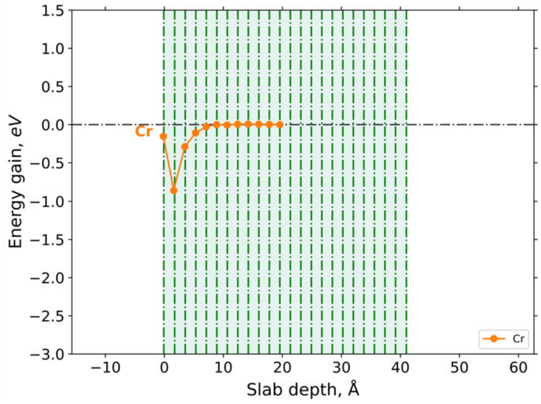
- He is slightly repeled by surface, but favorable inside vacuum
- Li is also slighly repeled, but favorable at the surface
- Mg is attracted by surface
- Al is similar to Mg
- Si is the most favorable impurity at the surface
- Cr is attracted, but the most favorable position is in the first subsurface layer

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## Impurities near Be $(0001)$ surface

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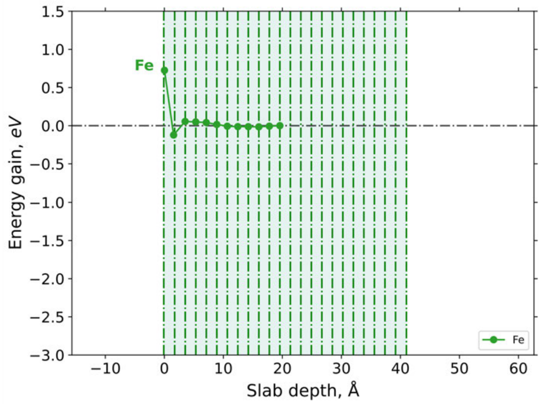
- Li is also slighly repeled, but favorable at the surface
- Mg is attracted by surface
- Al is similar to Mg
- Si is the most favorable impurity at the surface
- Cr is attracted, but the most favorable position is in the first subsurface layer
- Fe is unfavorable at the surface

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## Impurities near Be $(1\bar{1}00)$ surface

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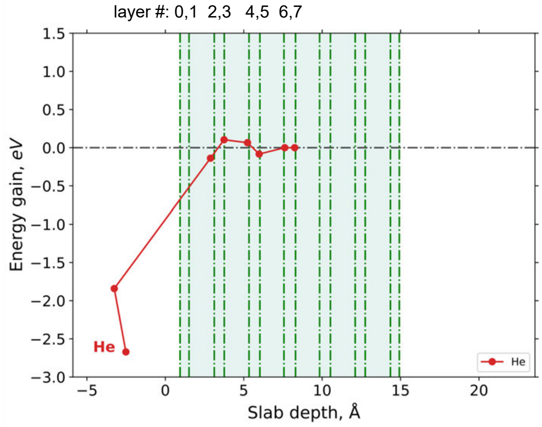
- He goes inside bubble from layers #0 & 1

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## Impurities near Be $(1\bar{1}00)$ surface

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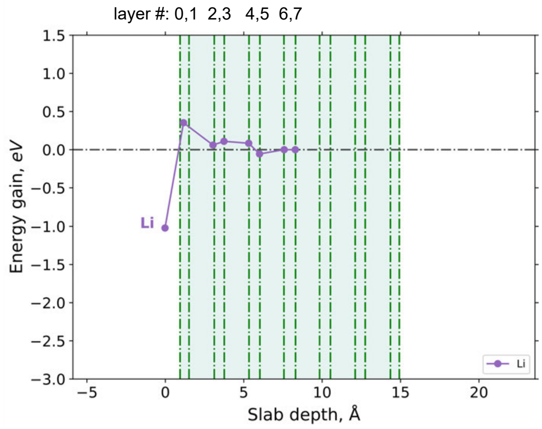
- He goes inside bubble from layers #0 & 1
- Li is also slighly repeled, but favorable at the surface

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## Impurities near Be $(1\bar{1}00)$ surface

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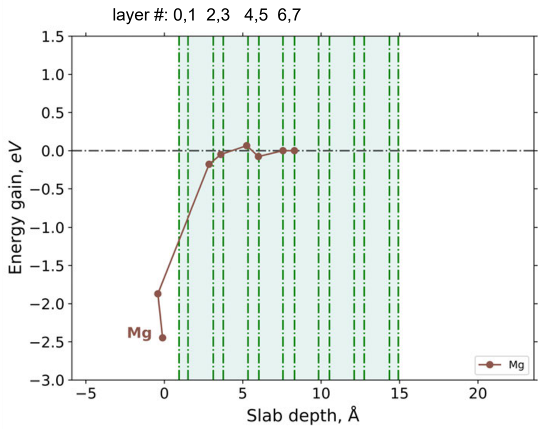
- He goes inside bubble from layers #0 & 1
- Li is also slighly repeled, but favorable at the surface
- Mg goes to the surface from layers #0 & 1

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## Impurities near Be $(1\bar{1}00)$ surface

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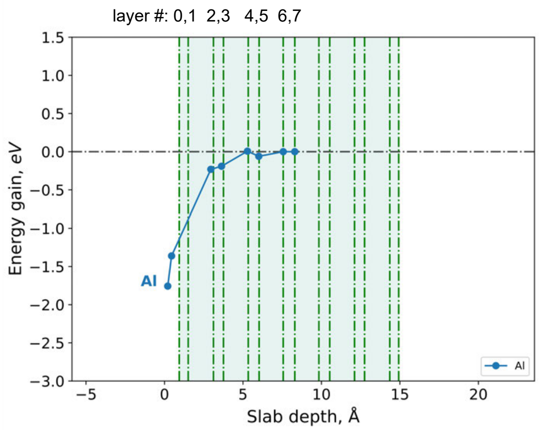
- He goes inside bubble from layers #0 & 1
- Li is also slighly repeled, but favorable at the surface
- Mg goes to the surface from layers #0 & 1
- Al is similar to Mg

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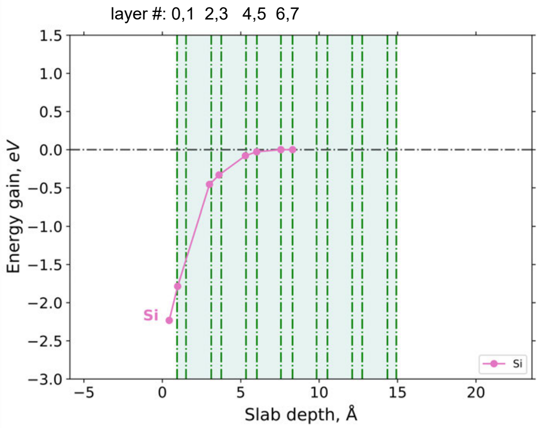
- Al is similar to Mg
- Si is the second favorable impurity at the surface after Mg

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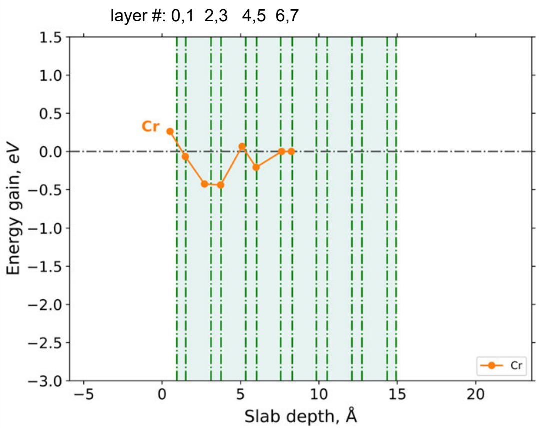


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## Impurities near Be $(1\bar{1}00)$ surface

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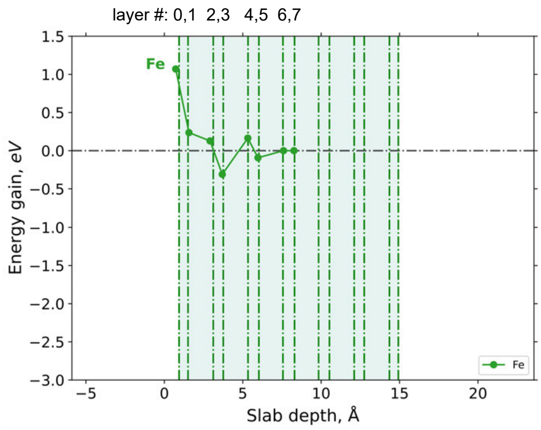
- Mg goes to the surface from layers #0 & 1
- Al is similar to Mg
- Si is the second favorable impurity at the surface after Mg
- Cr is slightly unfavorable at the surface, but favorable at subsurface layers #2 & 3
- Fe is unfavorable at the surface, but slightly favorable at subsurface layer #3

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## Interaction of impurities with surfaces

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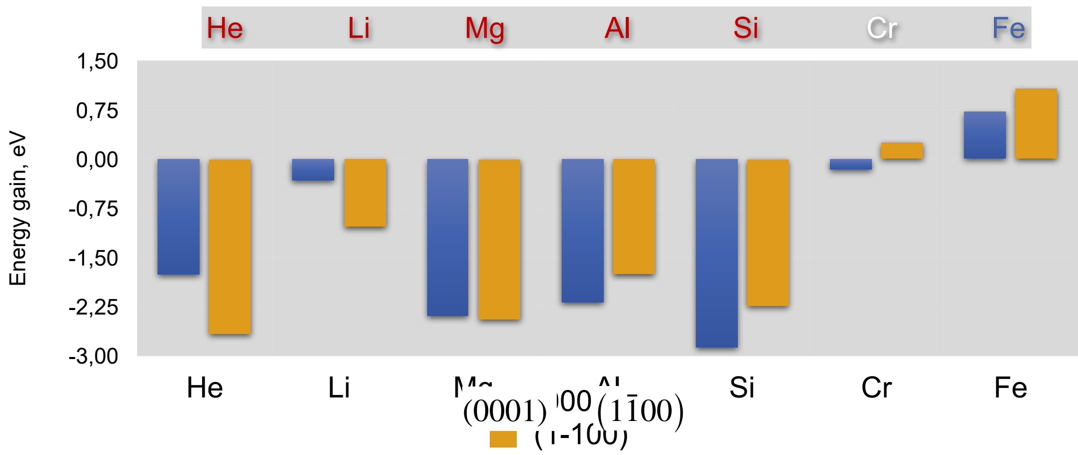


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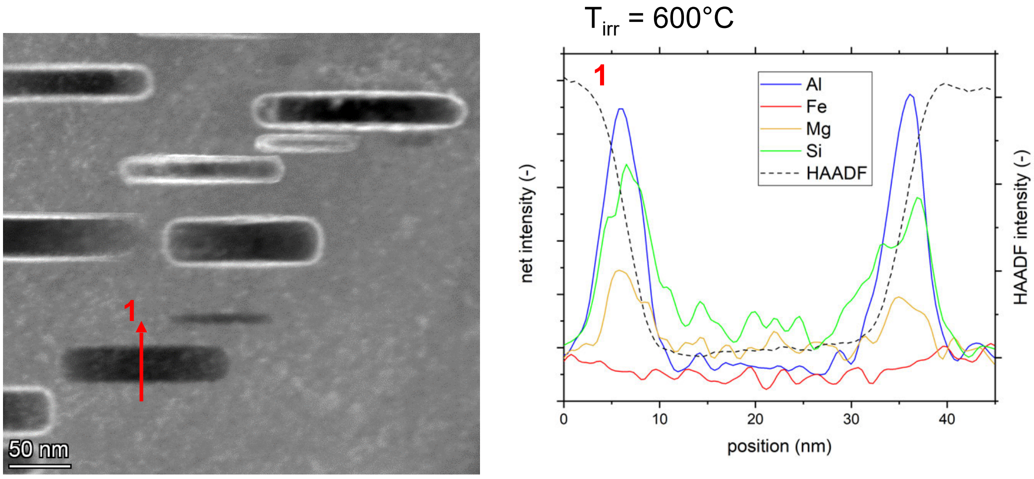
## Comparision with experiment

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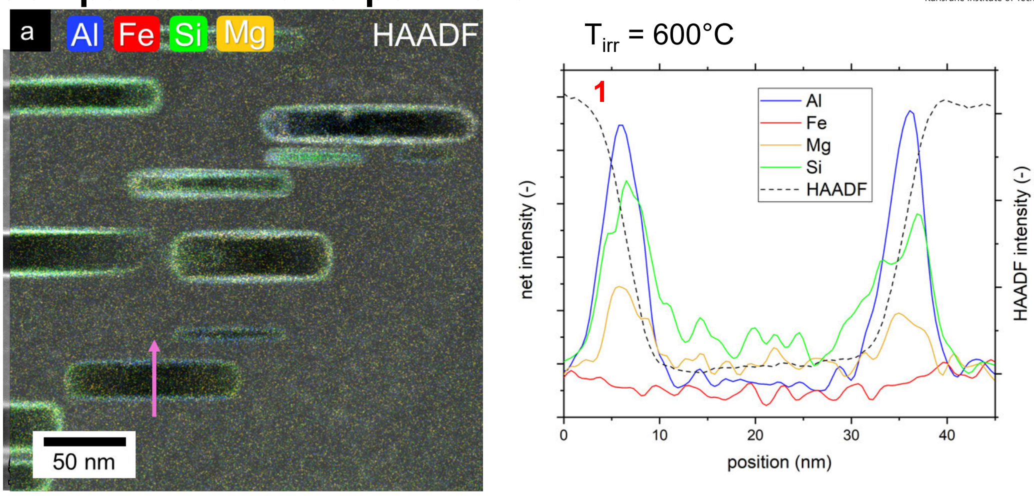
## Comparision with experiment

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## Comparision with experiment

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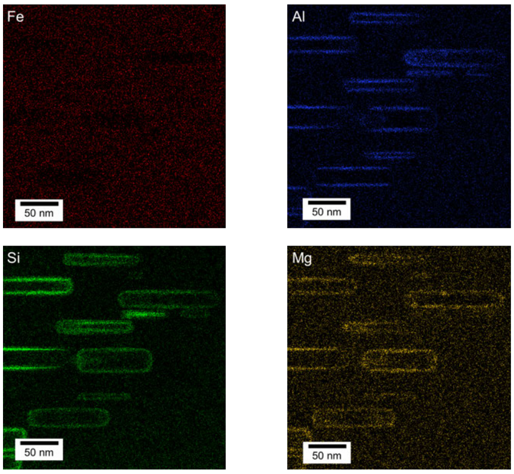


- Fe is homogeneously distributed over beryllium matrix
- Al, Si and Mg cover surfaces of helium bubbles

$T_{irr}$ = 600°C

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## Conclusions

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- DFT caclulations suggest that
  - there is a correlation between interaction of solutes with vacancies, surfaces and self-interstitials: those which have binding with vacancies are also attracted by free surfaces and repelled by self-interstitials.
  - Mg, Al, Si have positive binding with vacancies and free surfaces
  - Cr and Fe have no binding with vacancies, also have no binding or even slightly repeled by surfaces, but have attraction to SIAs
- Consequences for diffusion mechanisms
  - Fe and Cr migrate against vacancy gradient
  - Si and Al migrate along vacancy gradient as Solute-Vac complex (e.g. to bubbles or dislocations)
- These findings were confirmed experimentally using TEM equipped with EDX:
  - formation of Mg, Al, Si enriched zones anround gas bubbles in beryllium under irradiation.
  - formation of gas bubbles on $FeAlBe_4$ precipitates as a consequence of Vac-Al complex diffusion
- Obtained results will be used to evaluate the effect of impurities on gas bubble growth, swelling and tritium retention inside helium bubbles.

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