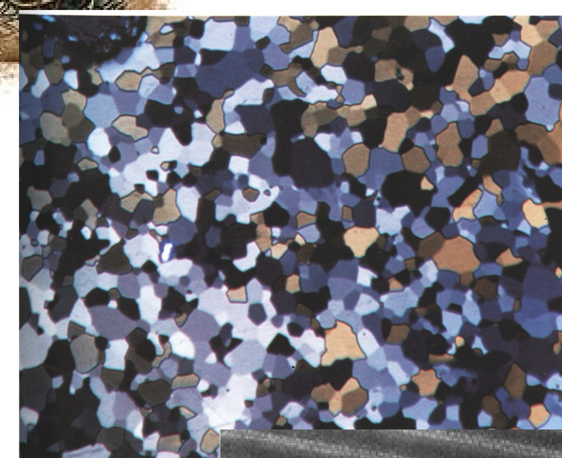
Effect of impurities on structural, cohesive, and magnetic properties of grain boundaries in α-Fe

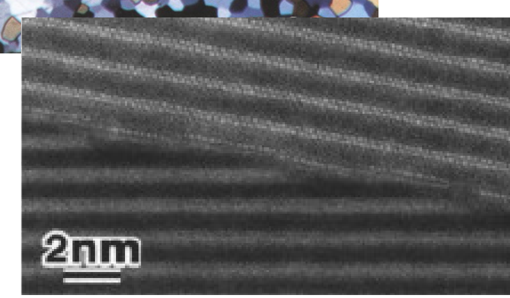
Elwira Wachowicz and Adam Kiejna

Institute of Experimental Physics, Univeristy of Wrocław, Wrocław, Poland

Motivation

- most materials polycrystalline – grains
- grain size several nm to several mm
  - many macroscopic properties (e.g. strength, corrosion resistance) determined by grain boundaries properties
- impurities diffuse towards grain boundaries → modify grain boundaries and materials properties





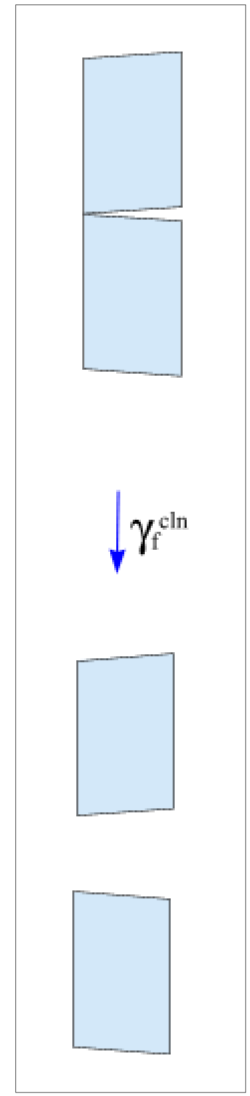
- New challenges for steels
- **Relatively few experiments – theory could help**

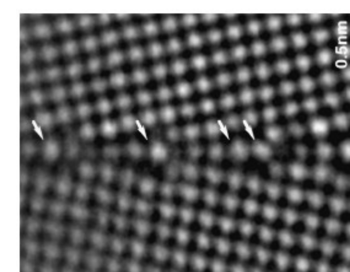
Grain boundary cohesion

Adhesive binding energy:

$$\gamma_f = E_{GB} - 2E_{FS}$$

- γ_f of the order of several eV
- Structural relaxation: reduction of the total energy (Fe Σ3: by 1.61 eV/cell)
- Symmetric and asymmetric GBs





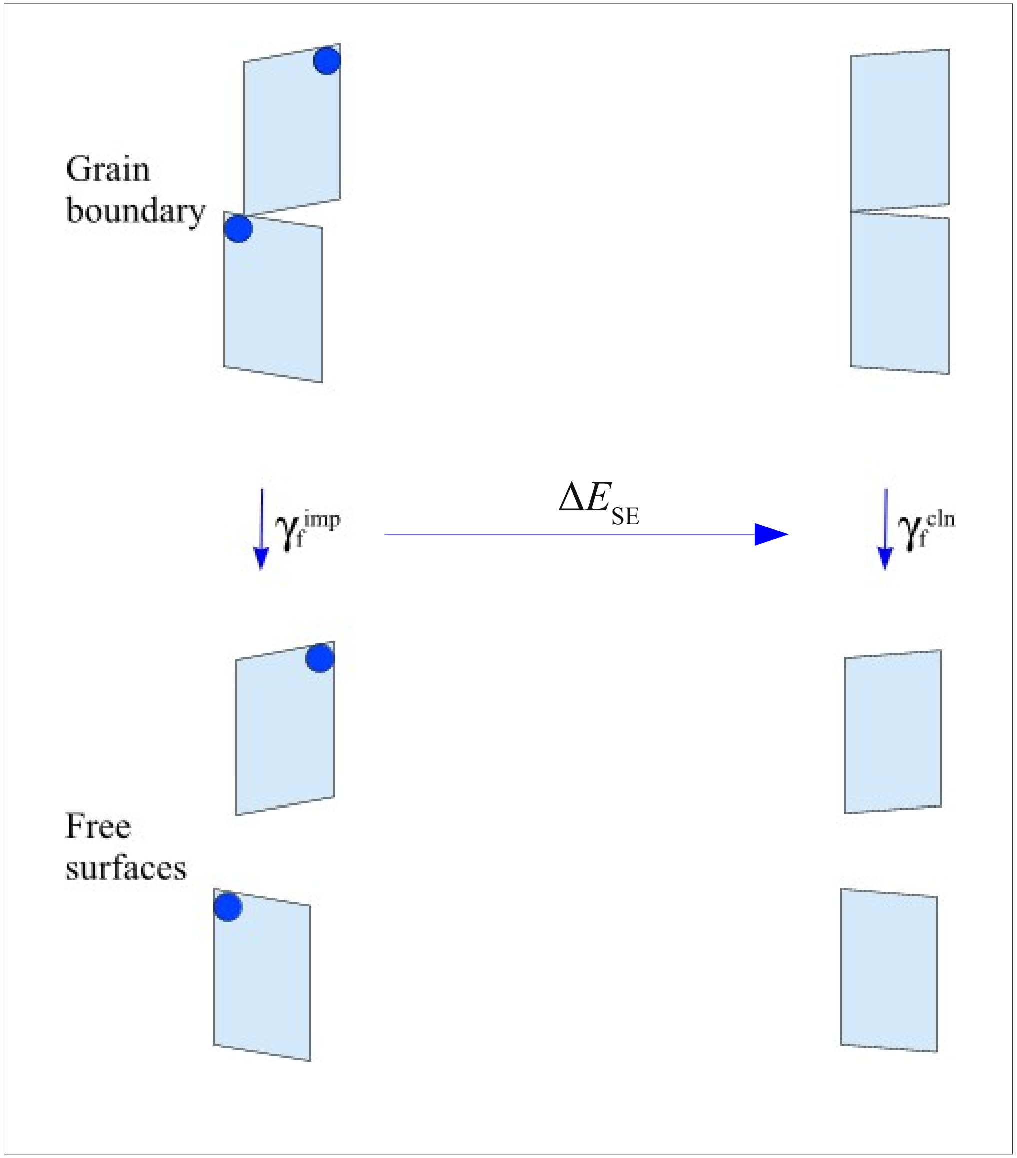
J. R. Rice and J.-S. Wang, Mater. Sci. Eng., A **107**, 23 1989.

The strengthening energy:

$$\Delta E_{SE} = \gamma_f^{imp} - \gamma_f^{cln}$$

$\Delta E_{SE} > 0 \rightarrow$ embrittler

$\Delta E_{SE} < 0 \rightarrow$ cohesion enhancer



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The strengthening energy

The strengthening energy:

$$\Delta E_{\mathrm{SE}} = \gamma_{\mathrm{f}}^{\mathrm{imp}} - \gamma_{\mathrm{f}}^{\mathrm{cln}}$$

The chemical component:

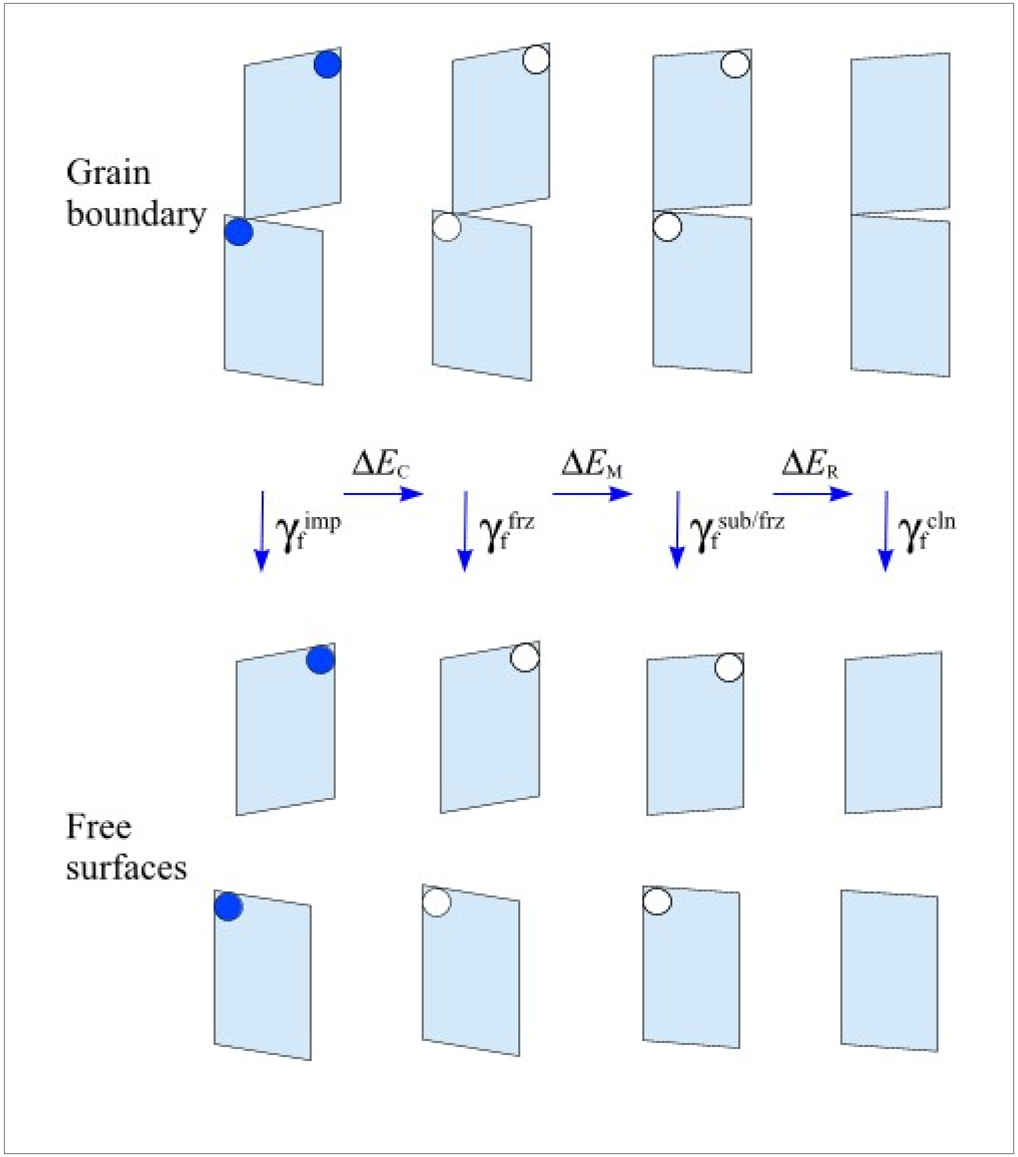
$$\Delta E_{\mathrm{C}}$$

The mechanical component:

$$\Delta E_{\mathrm{M}}$$

The host removal component:

$$\Delta E_{\mathrm{R}}$$



$\Delta E_{SE} >$ → embrittler; $\Delta E_{SE} < 0$ → cohesion enhancer

Total energy calculations

- Density functional theory (VASP)
- Spin-polarized GGA PW91
- Plane waves basis
- PAW method potentials
- Supercells
- Full optimisation of both supercell and atomic positions

Clean Fe GBs supercell

Σ3(111)

Tilt angle: 70.5°

1x1 cell:

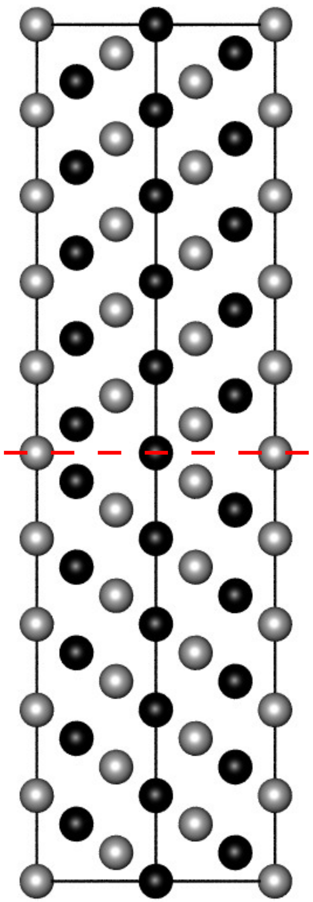
30 atoms

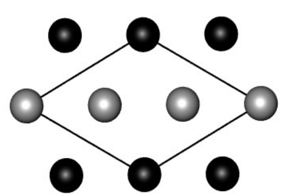
2x2 cell:

120 atoms

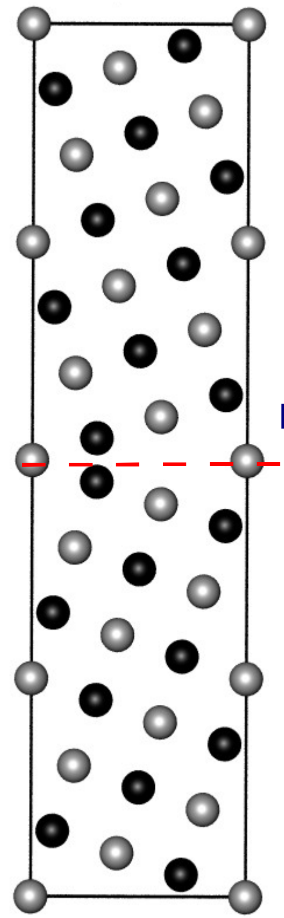
Adhesive binding energy:

γ_f = -3.78 J/m^2

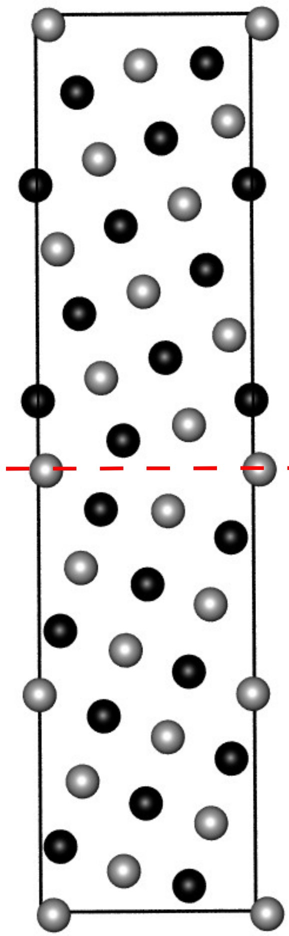


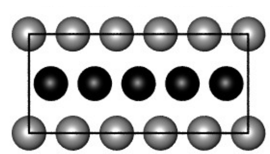


Σ5(210)



relaxation





Tilt angle: 53.1°

1x1 cell:

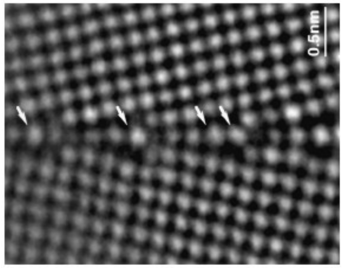
40 atoms

1x2 cell:

80 atoms

Adhesive binding energy:

γ_f = -3.19 J/m^2



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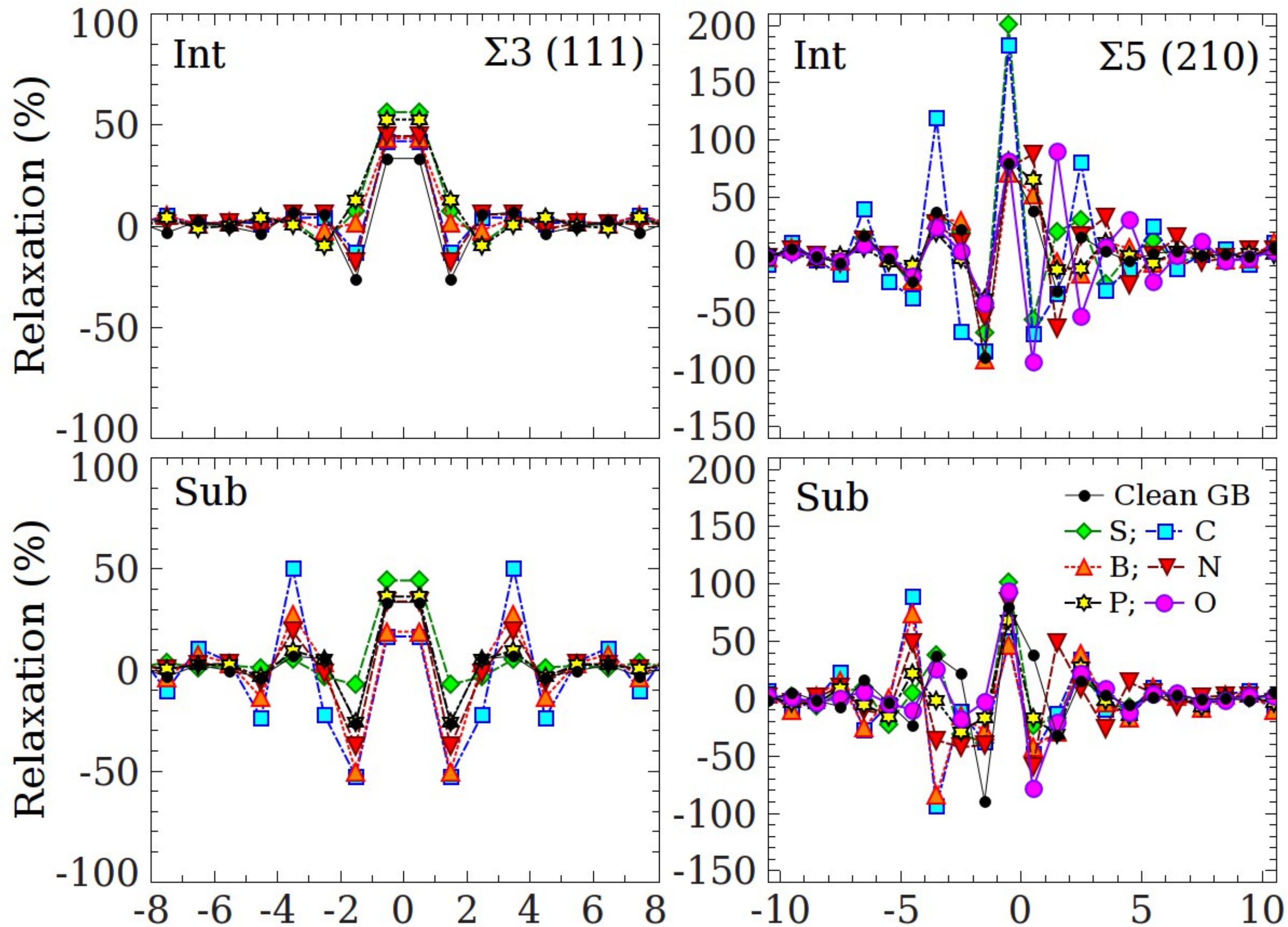
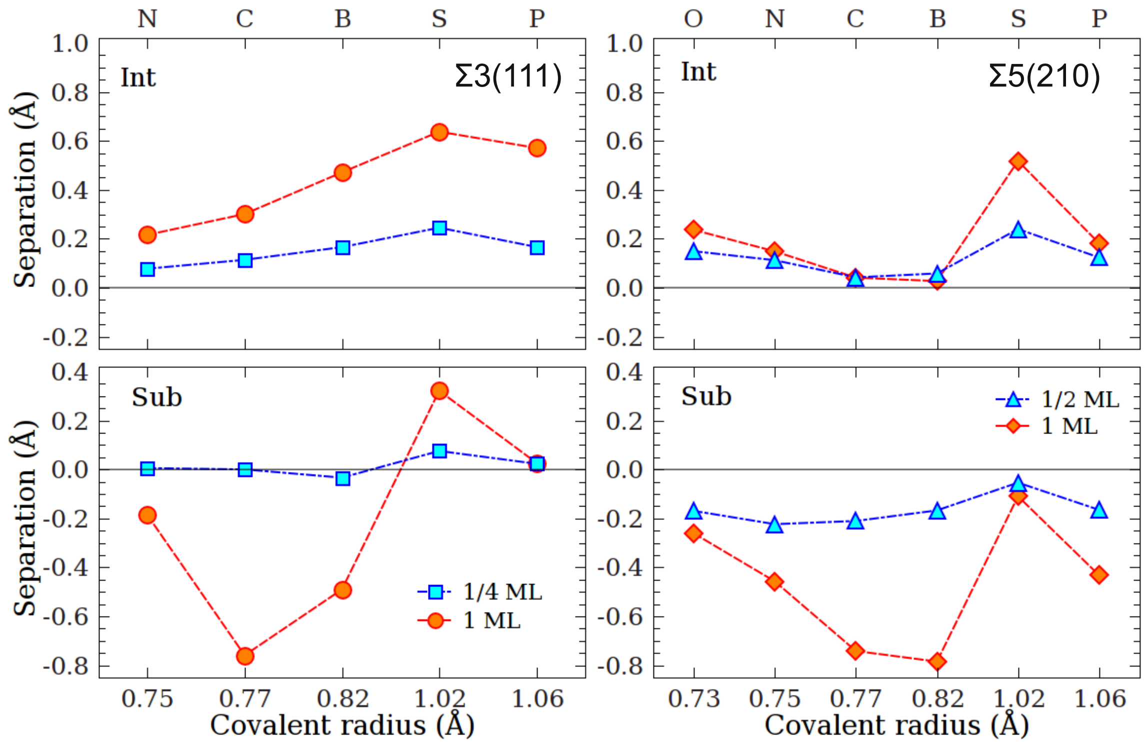
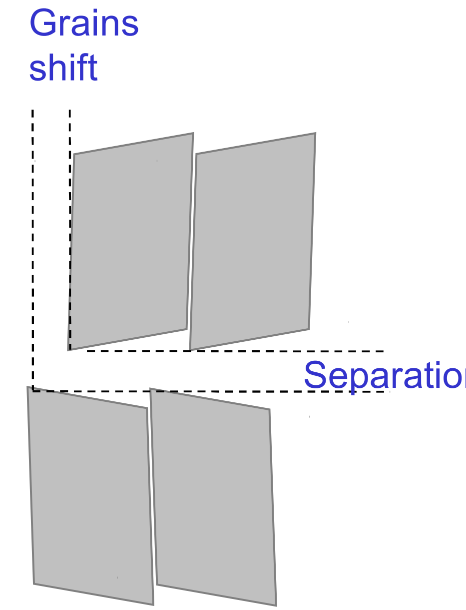
Relaxations



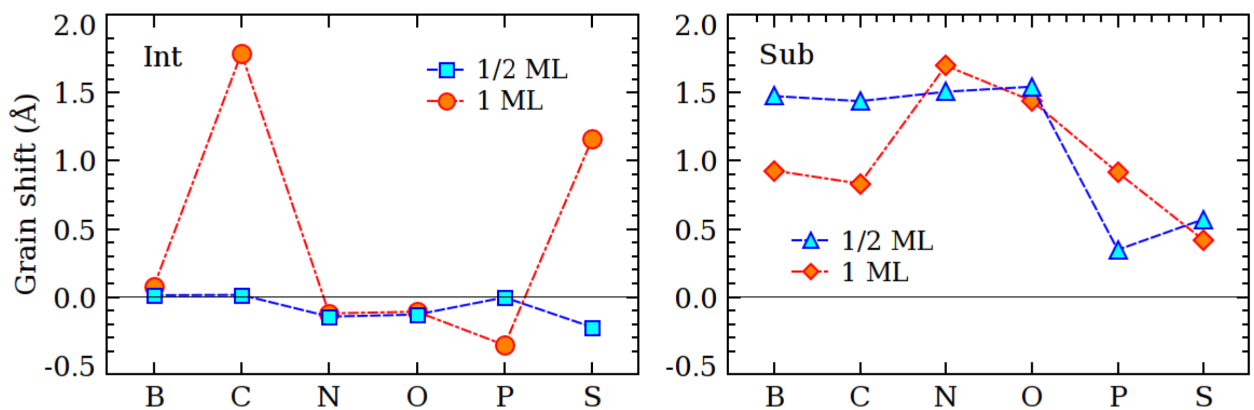
- Relaxations much higher (up to 200%) than at surfaces.
- For interstitial impurities the largest increase for the largest atoms.
- B & C – long-range distortion in the bulk (Jiang, Carter, PRB **67** (2003) 214103.)

Geometry changes

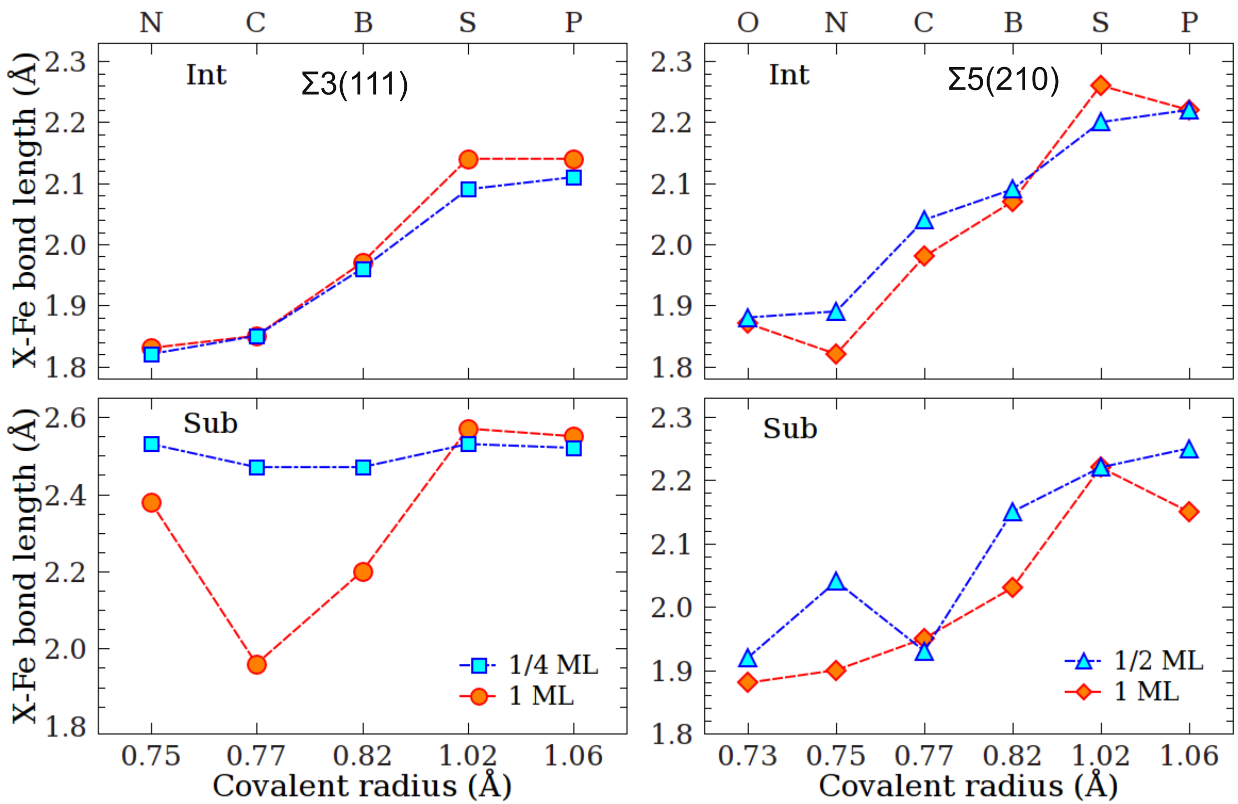




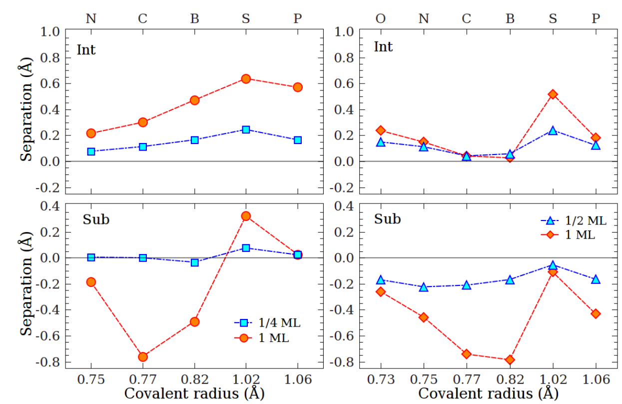
Shifts allow the grains to come into the closest contact and form more stable interface.



Bond lengths



The radii of all impurities are smaller than that of Fe – a similar character of variation with impurity.

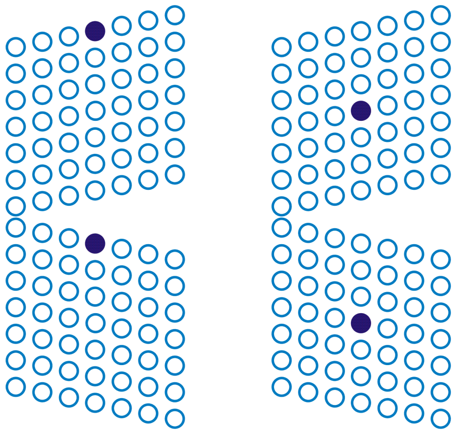


Small concentrations of impurities do not affect the Fe-Fe bonding – constant bond length at FeΣ3.

At ML concentration a substitution means a replacement of whole Fe layer.

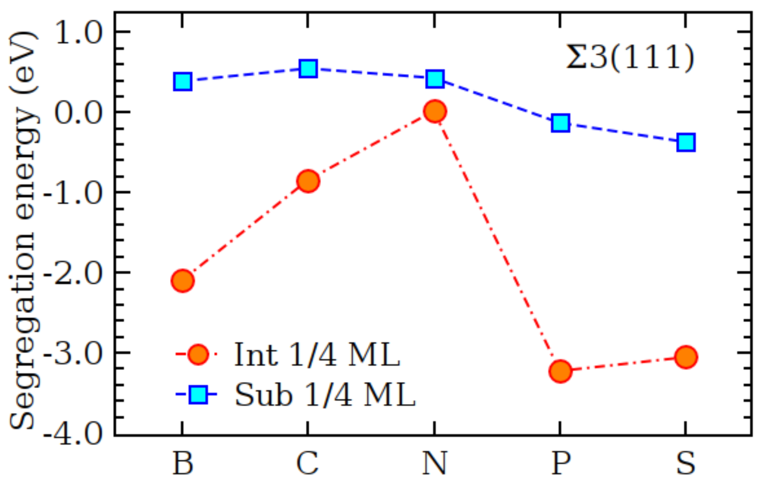
Different behaviour at the Fe Σ5(210) GB. Grains are brought to a closer contact due to the grains' shift and small sizes of impurities.

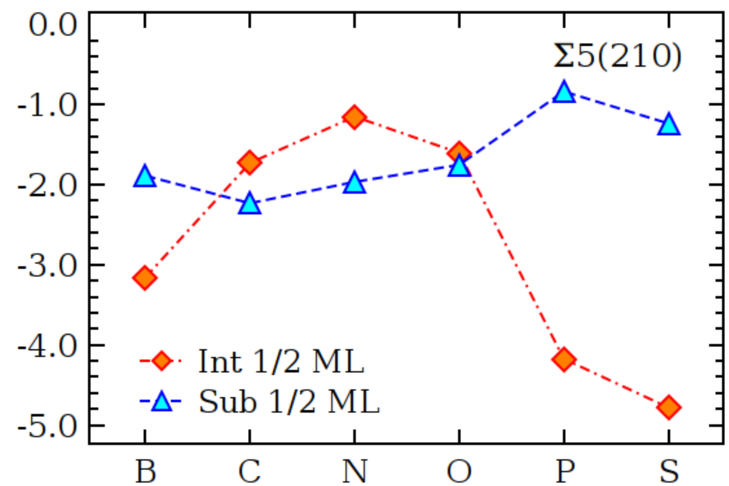
Segregation



$$E_{\text{segr}} = E_{\text{X,GB}} - E_{\text{X,bulk}}$$

$E_{\text{segr}} < 0$ favors segregation

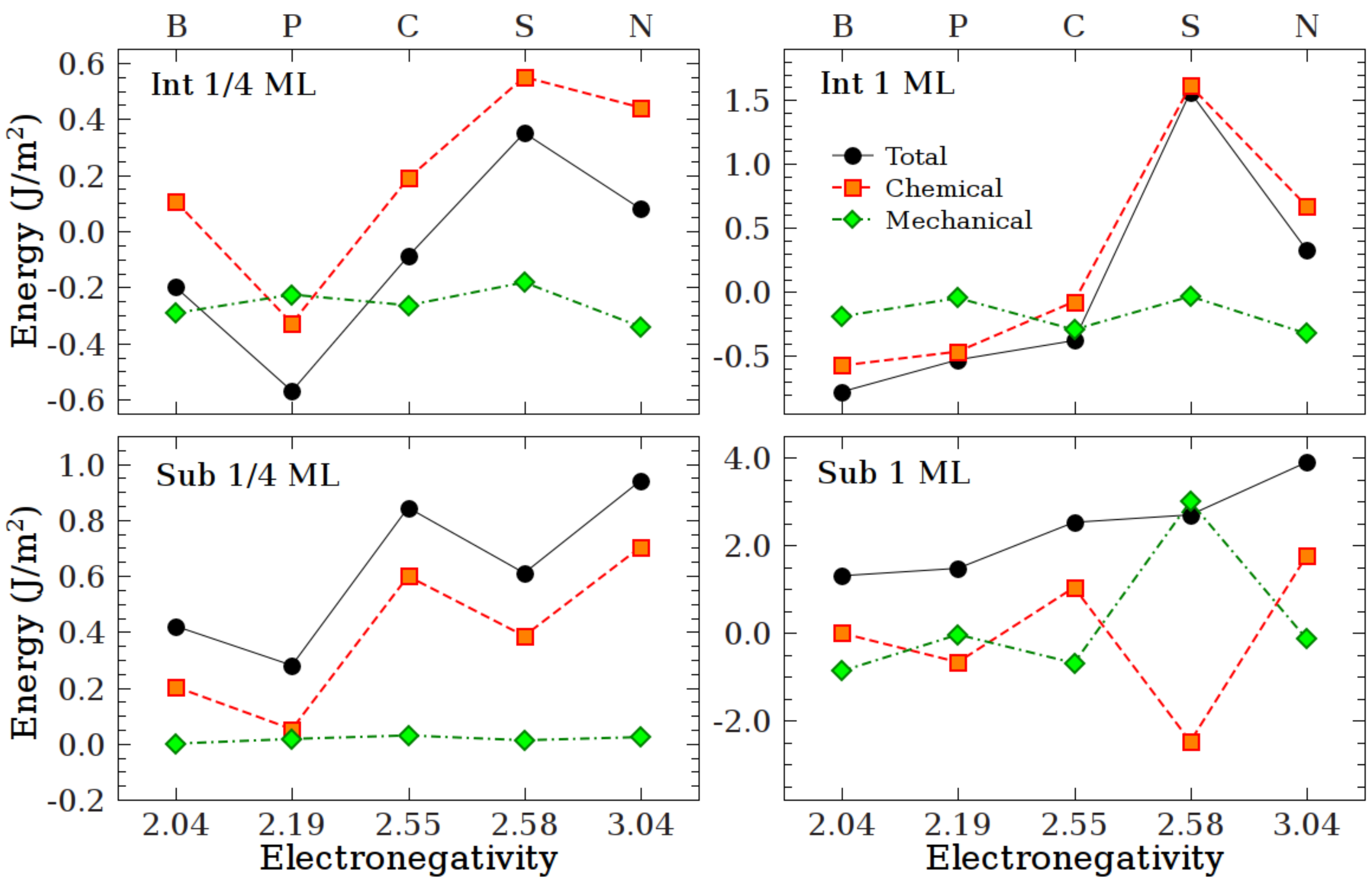




Interstitial impurities segregate at Fe Σ3

Impurities enrich the Fe Σ5 GB

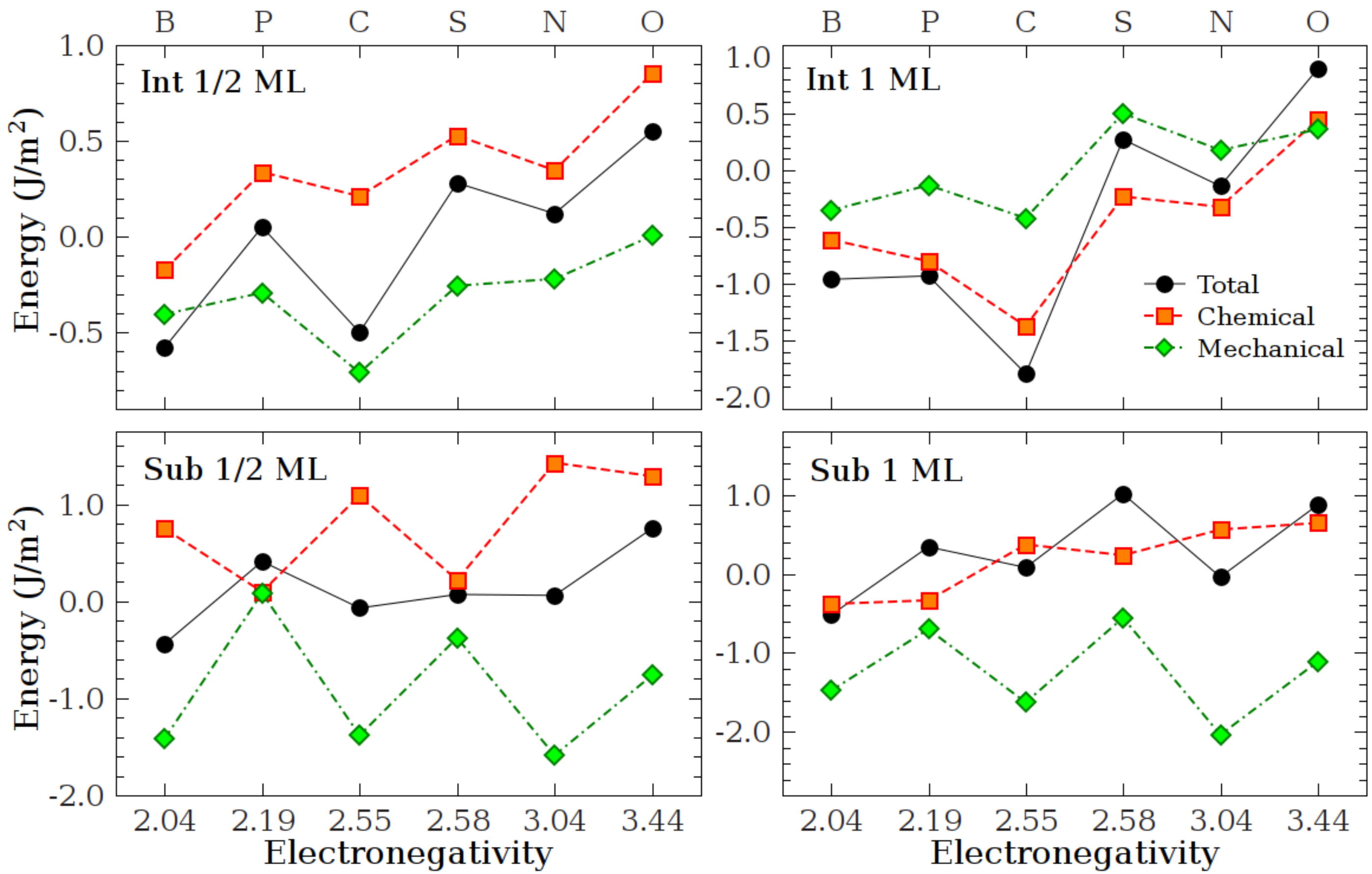
Strengthening/embrittlement Σ3(111)



Interstitial B, P, and C are cohesion enhancers at Σ3 GB.

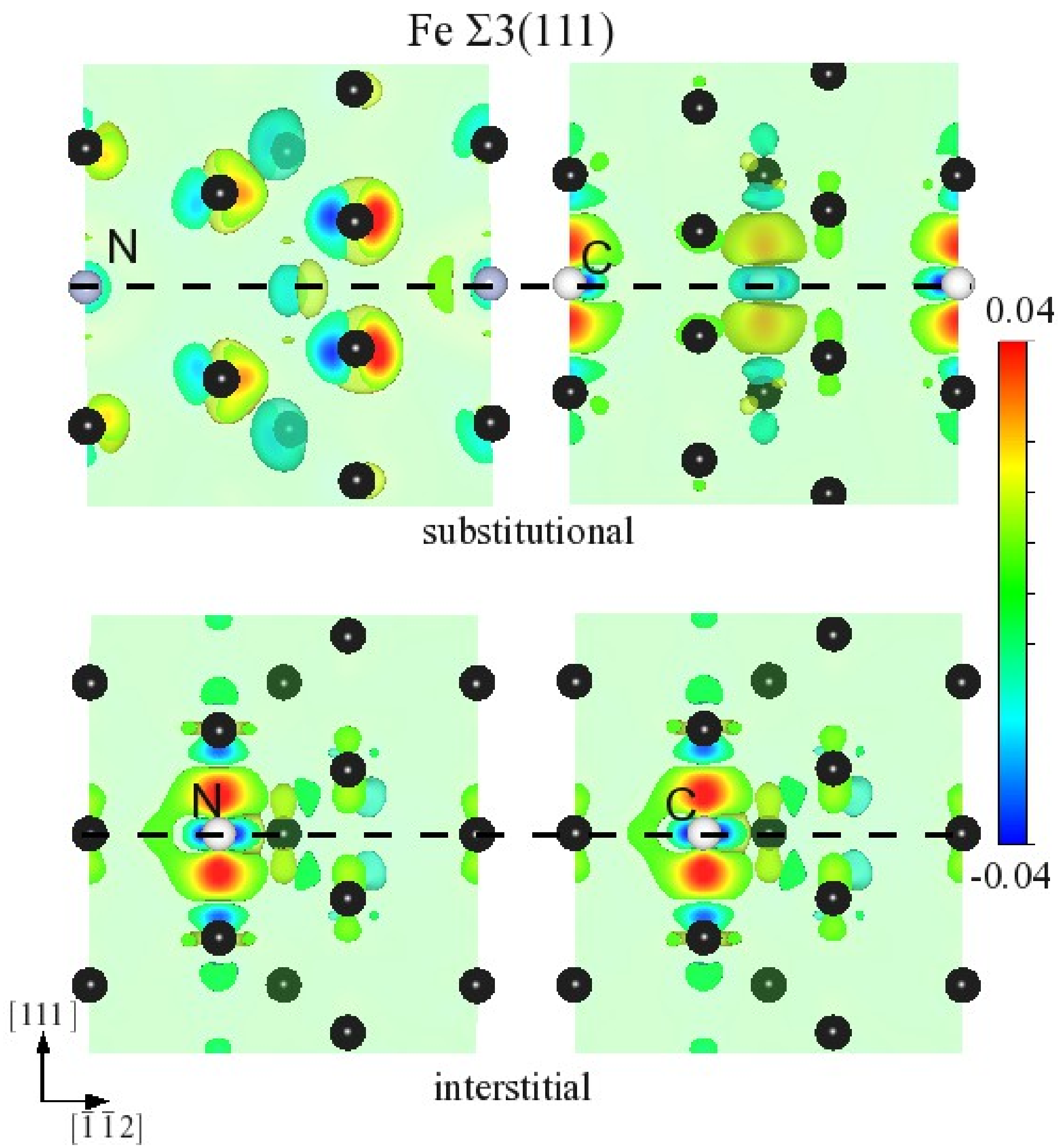
All substitutional impurities act as embrittlers at Σ3 GB.

Strengthening/embrittlement Σ5(210)



- Boron at each concentration is the only impurity which strengthens Fe Σ5(210) GB.
- Substitutional C and N, at low and high concentrations respectively, are weak enhancers.
- Strong embrittling effect of oxygen and sulphur.

Charge density differences: Σ3(111)

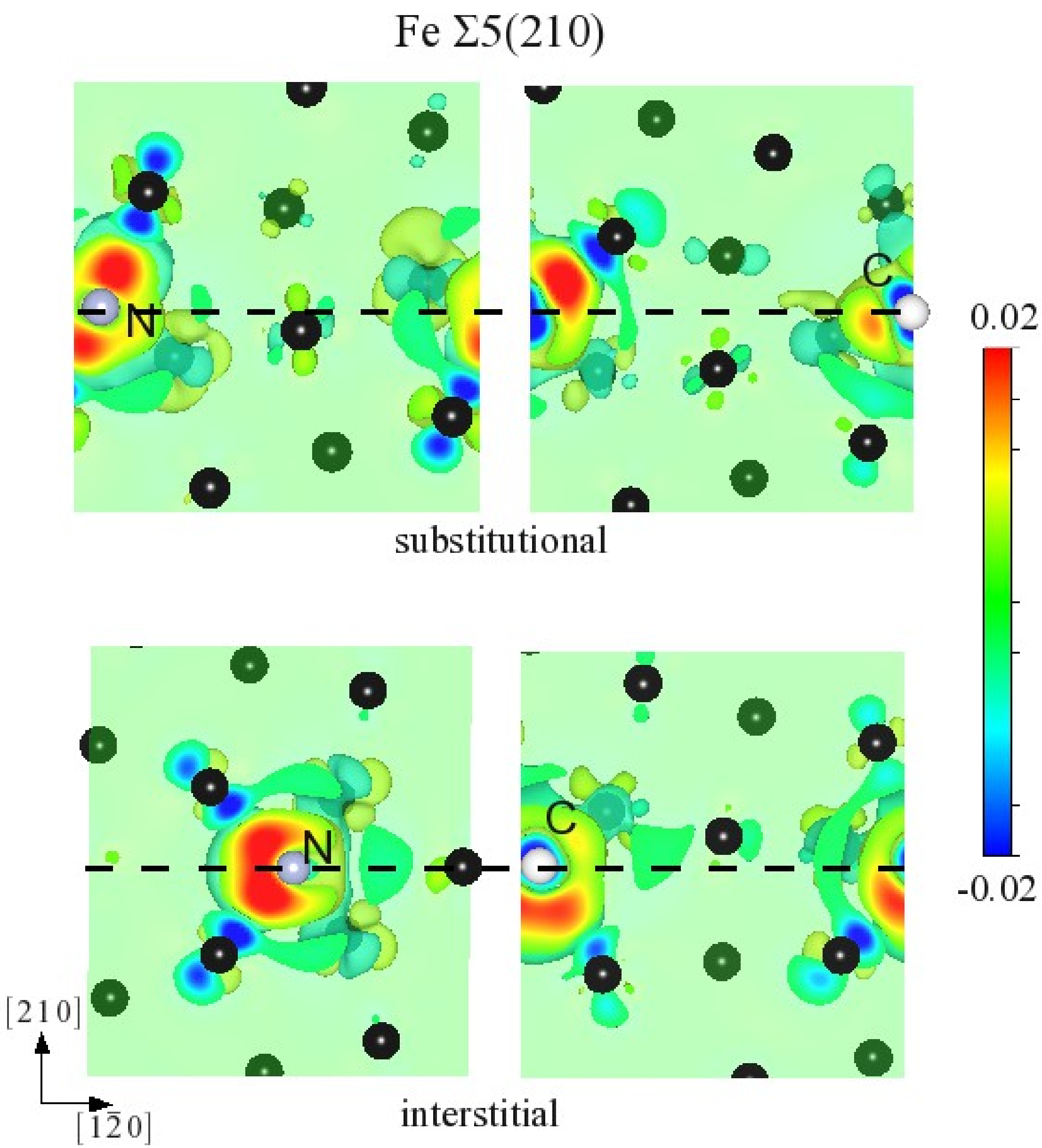


Both impurities reduce adhesion.

The weakening is much stronger for nitrogen – deficiency of the electron charge in the GB plane.

For carbon the charge density changes in the direction perpendicular to the GB.

Charge density differences: Σ5(210)



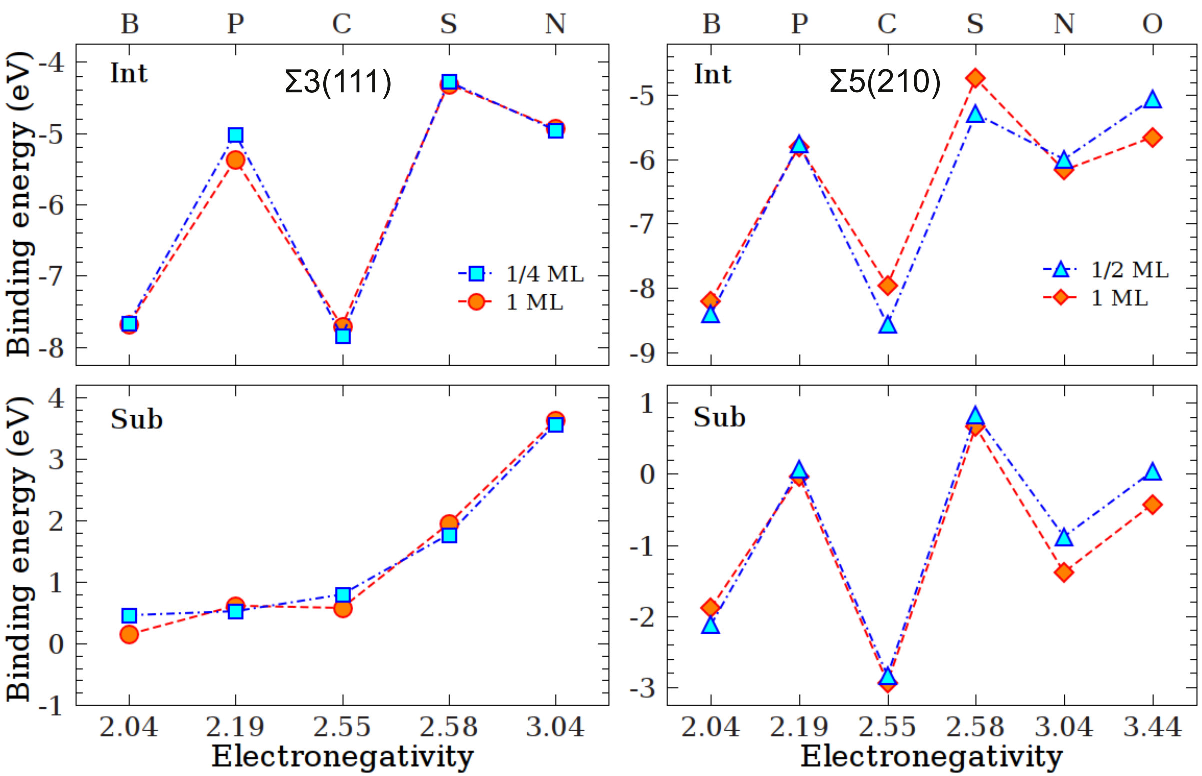
Small difference for nitrogen and carbon (reflected also in small differences of their chemical components).

A stronger interaction of carbon than nitrogen with Fe host atoms.

Binding energy

$$E_b = (E^{X/GB} - E^{GB} - 2E^X)/2$$

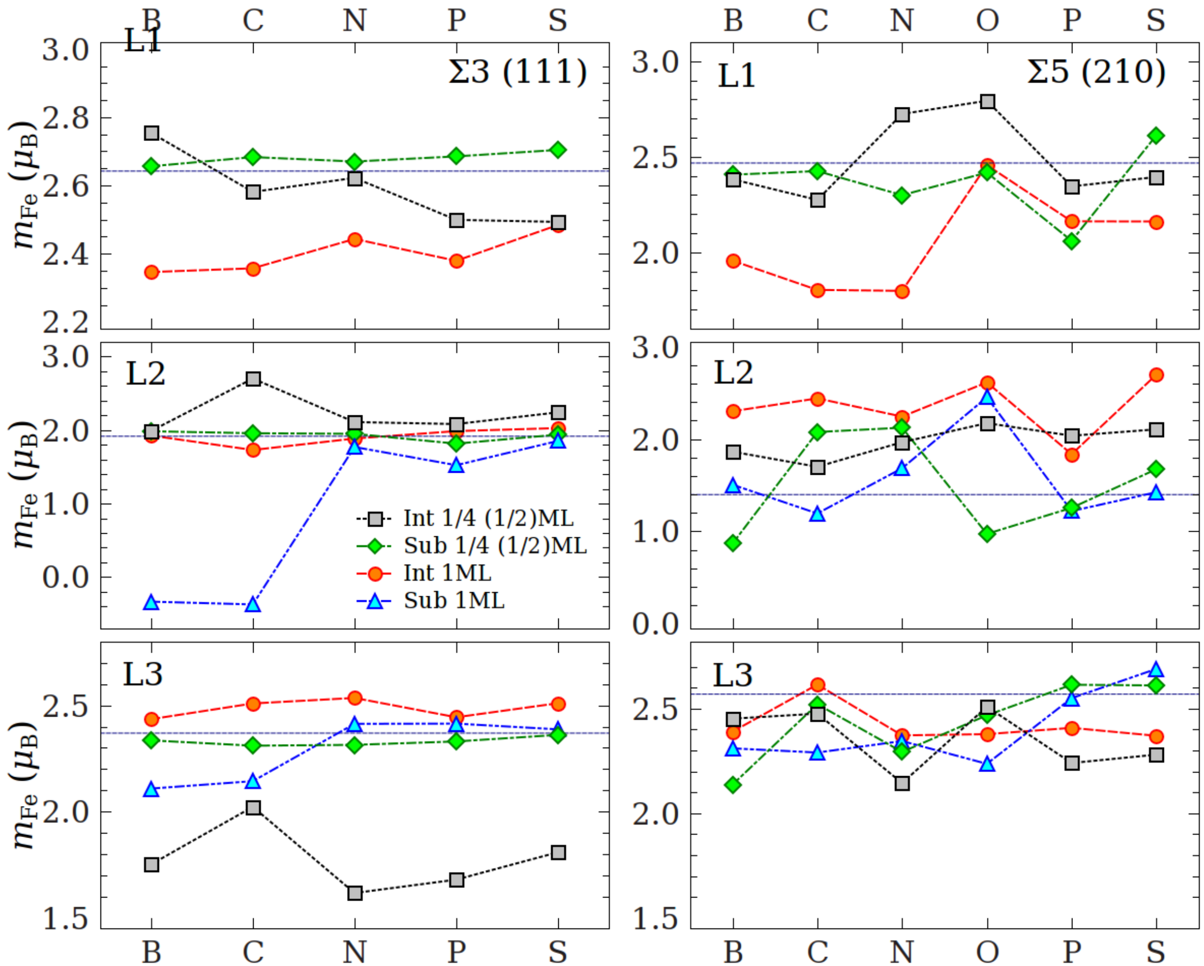
$E_b > 0$, impurity does not bind



Fe electronegativity: 1.83

- The difference between E_b for low and high impurity concentration is small.
- The binding decreases with increasing electronegativity.
- The larger electronegativity difference (the more polar bond) the stronger embrittling effect.
- Substitutional impurities at the Σ3 GB are highly unlikely.

Magnetic moments



M_{Fe} are increased compared with the bulk Fe (2.24 μ_B), to 2.7 μ_B at Σ3 GB, and to 2.53 μ_B at Σ5 GB.

Boron and carbon turn M_{Fe} to negative values – locally Fe becomes ferrimagnetic.

- Interstitial impurities influence the M_{Fe} stronger than substitutional ones.
- The moments on impurity atoms are in general negative and small (~ 0.1 μ_B).

Summary

- Large relaxation of atomic positions at the GBs.
- Interstitial impurities increase grains' separation, substitutional ones decrease it.
- All considered impurities segregate at Fe Σ5 GB, while Σ3 GB is enriched only by interstitial species, and substitutional P and C – more open GB favours segregation.
- In most cases the considered impurities act as embrittlers.
- Interstitial B, P, and C strengthen the Σ3 GB cohesion, and B and C in both sites strengthen the Σ5 GB.
- Sulphur and oxygen act as embrittlers in all configurations.
- The magnetic moments on the impurities are very small and, in general are aligned antiparallel to moments on Fe atoms.

E. Wachowicz, A. Kiejna, Comput. Mater. Sci., **43** (2008) 736.

E. Wachowicz, A. Kiejna, submitted to Modelling Simulation Mater. Sci. Eng.

Bader analysis