Heterophase Interfaces

M. Ceriotti - MSE304

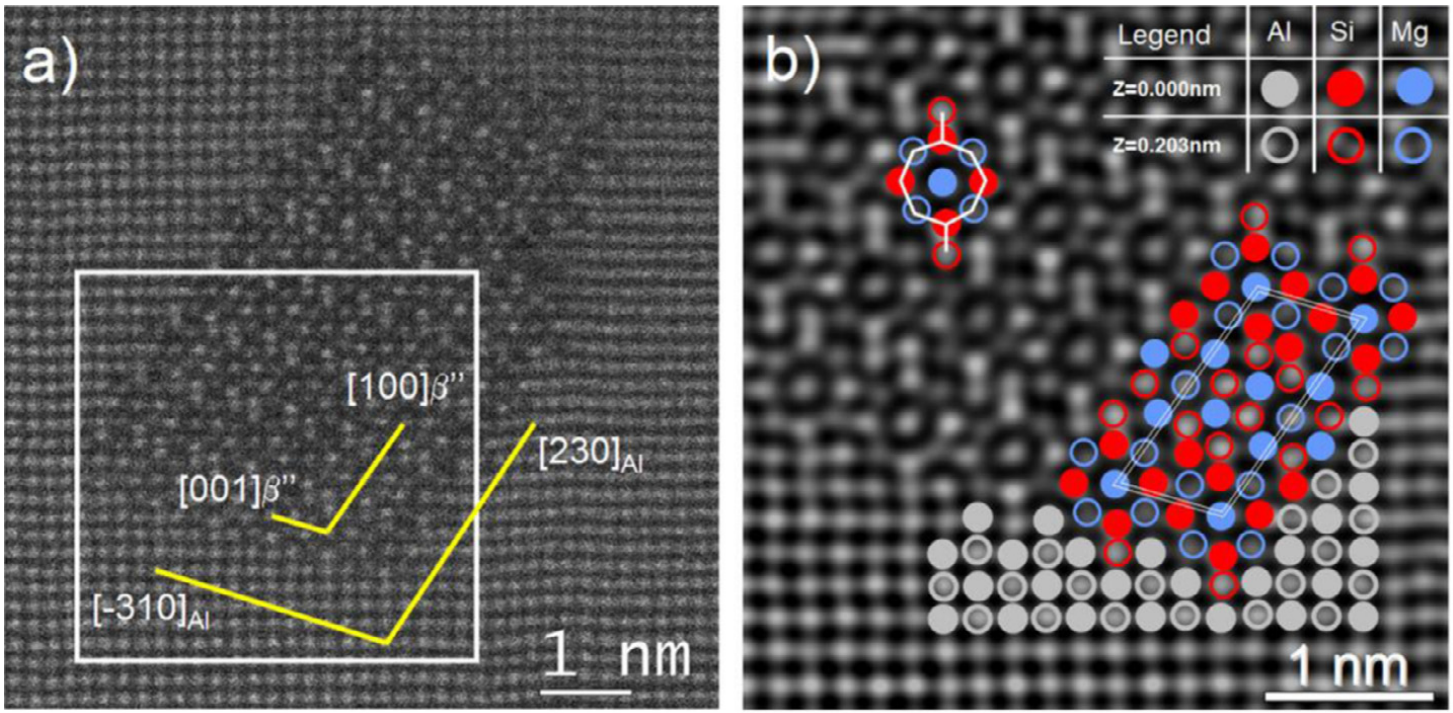
EPFL

Outline

- Atomistic perspective on interface energies
- The Becker model of heterophase interfaces
- Geometry of semicoherent interfaces
- Strain engineering in heteroepitaxial films

Heterophase interfaces

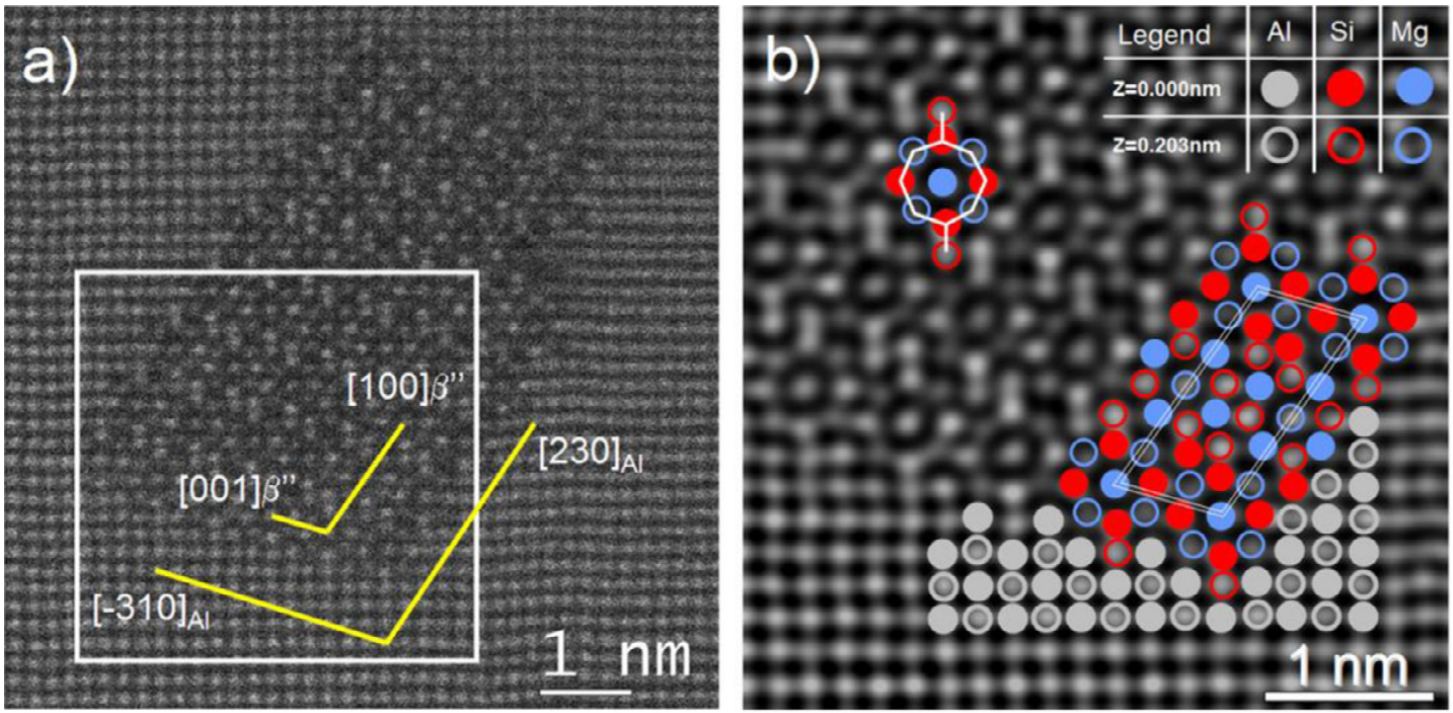
- An interface between two different compounds, or between different phases of the same compound.
  - Composition and/or lattice mismatch add an extra level of complexity
- One can distinguish coherent, semi-coherent or incoherent interfaces, depending on crystallographic mismatch and/or energetics



β'' precipitates in Al-Si-Mg alloys. [Ninive et al., Acta Materialia, 2014]

Heterophase interfaces

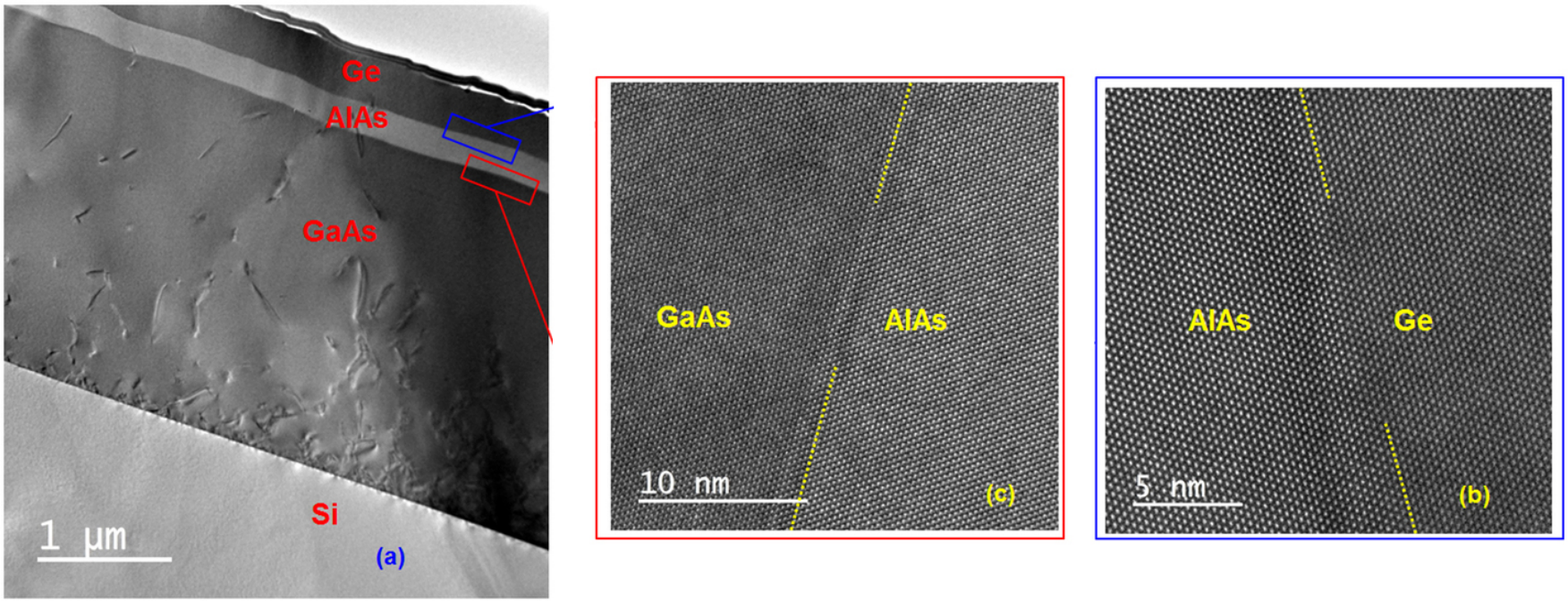
- An interface between two different compounds, or between different phases of the same compound.
  - Composition and/or lattice mismatch add an extra level of complexity
- One can distinguish coherent, semi-coherent or incoherent interfaces, depending on crystallographic mismatch and/or energetics



β'' precipitates in Al-Si-Mg alloys. [Ninive et al., Acta Materialia, 2014]

Heterophase interfaces

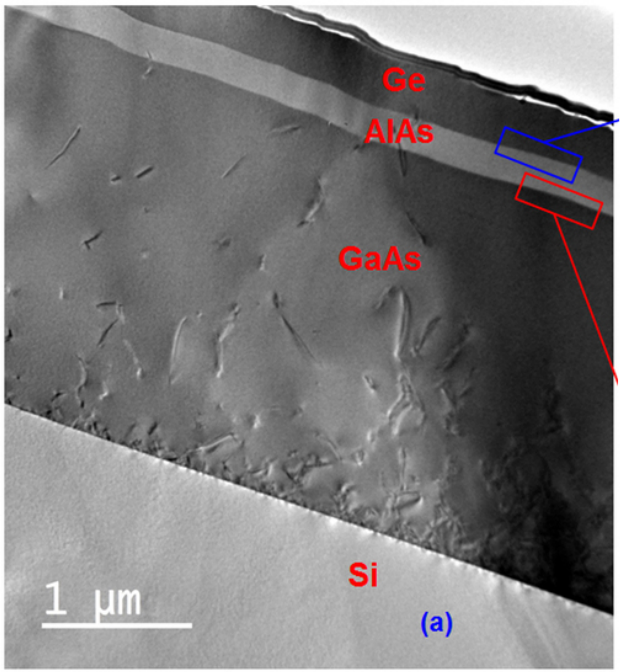
- An interface between two different compounds, or between different phases of the same compound.
  - Composition and/or lattice mismatch add an extra level of complexity
- One can distinguish coherent, semi-coherent or incoherent interfaces, depending on crystallographic mismatch and/or energetics

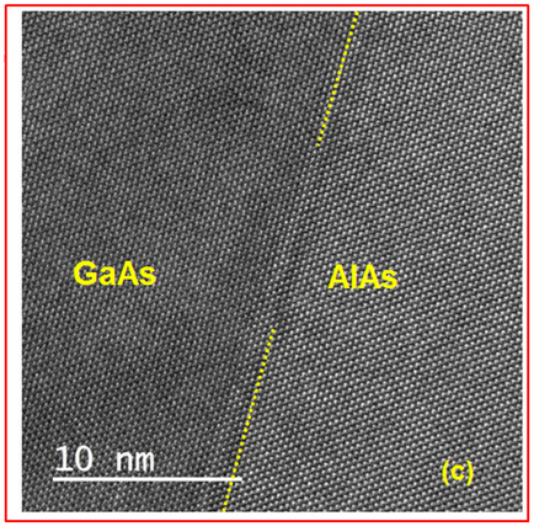


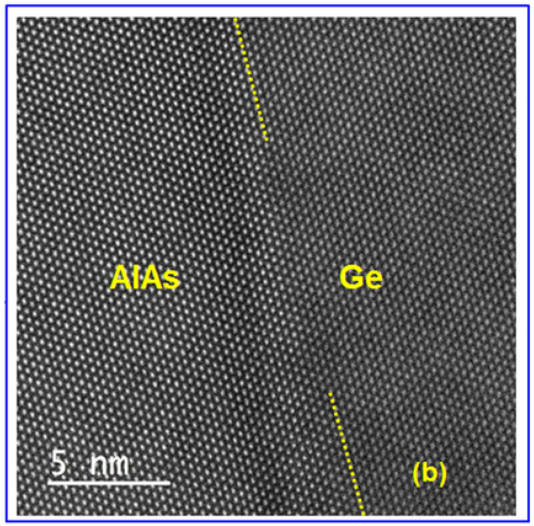
Epitaxial growth of semiconductors FET. [Hudait et al., Scientific Reports, 2014]

Heterophase interfaces

- An interface between two different compounds, or between different phases of the same compound.
  - Composition and/or lattice mismatch add an extra level of complexity
- One can distinguish coherent, semi-coherent or incoherent interfaces, depending on crystallographic mismatch and/or energetics



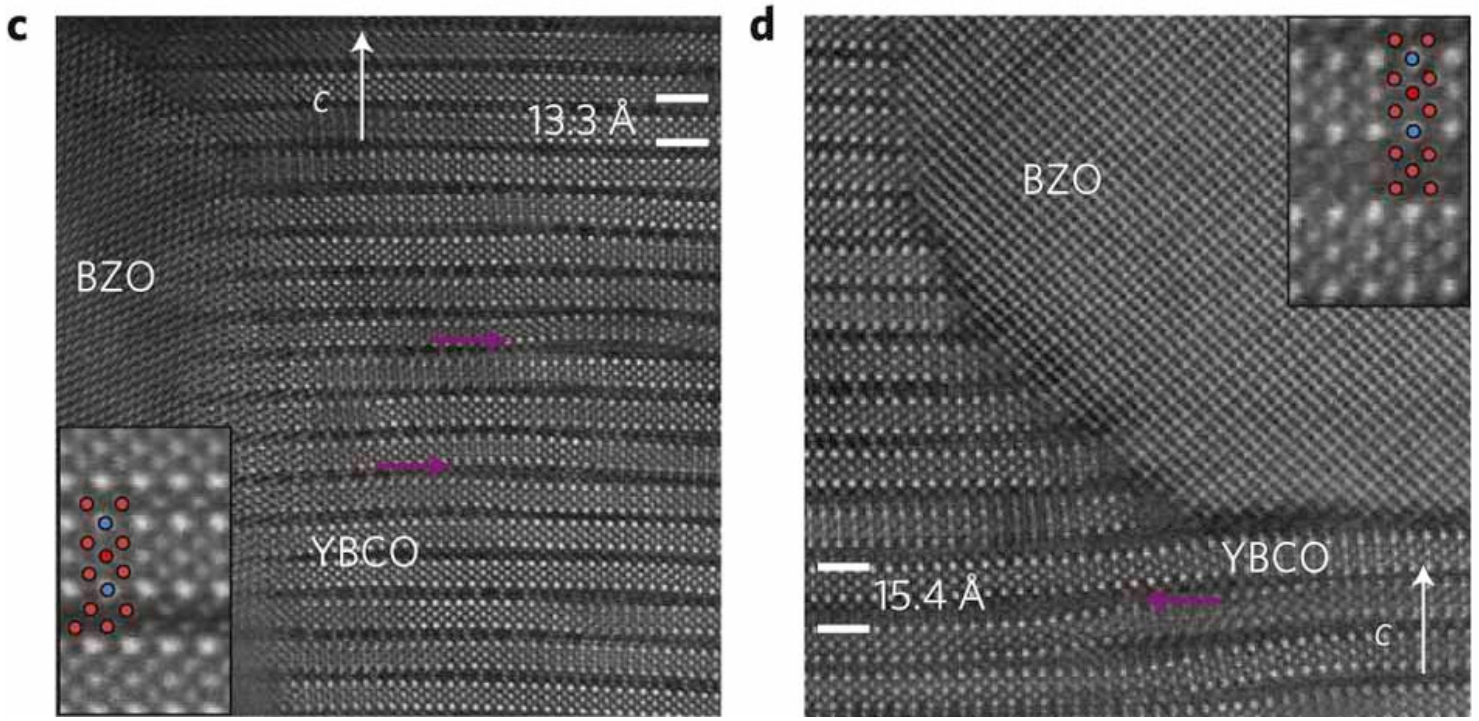




Lattice parameters: Si: 5.43Å, Ge: 5.65Å, GaAs: 5.65Å, AlAs: 5.66Å.

Heterophase interfaces

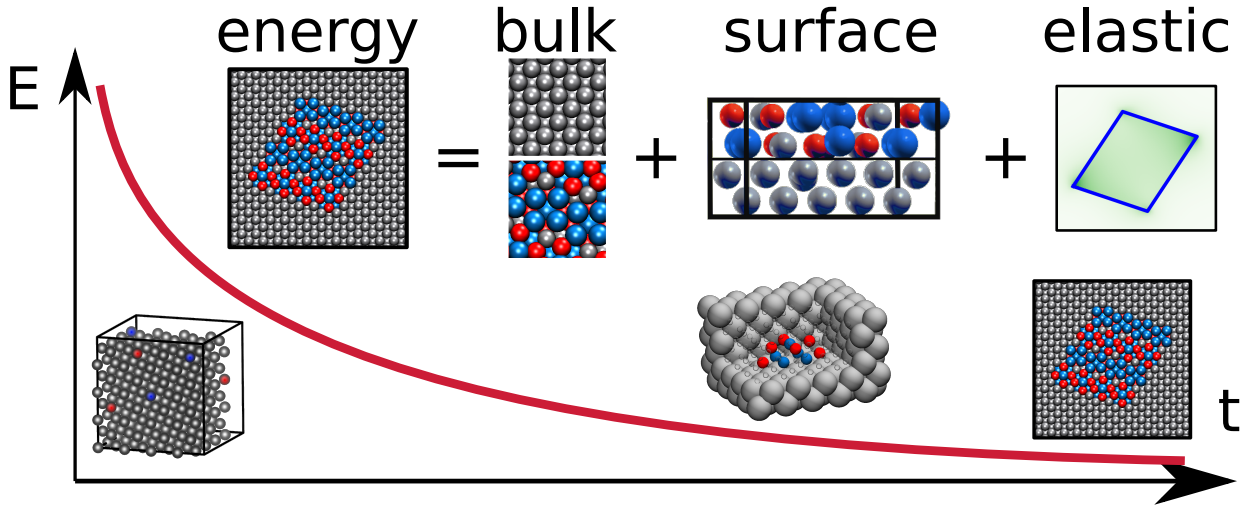
- An interface between two different compounds, or between different phases of the same compound.
  - Composition and/or lattice mismatch add an extra level of complexity
- One can distinguish coherent, semi-coherent or incoherent interfaces, depending on crystallographic mismatch and/or energetics



Barium zirconate nanoparticles in YBCO. [Llordés et al., Nature Mat. 2012]

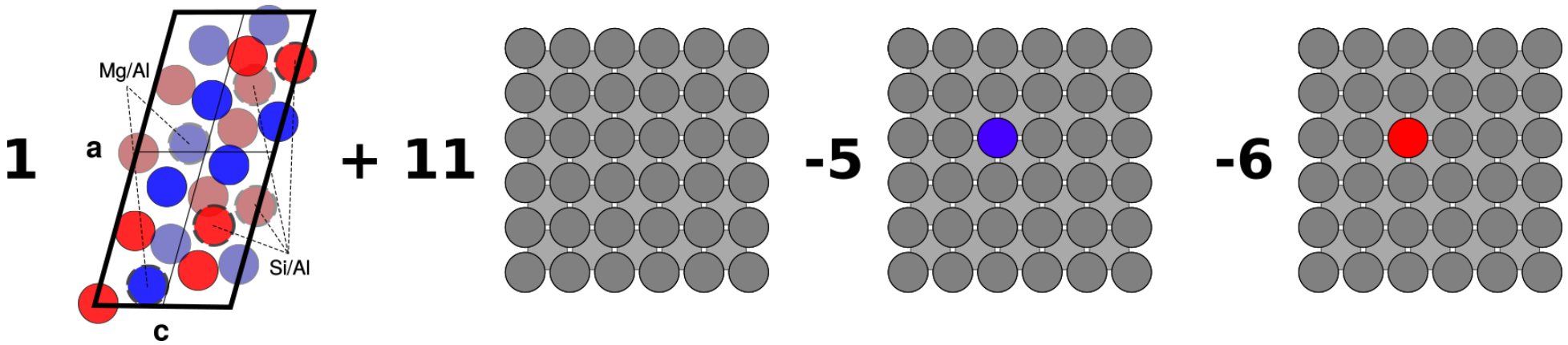
Precipitates in Al-6xxx - A Worked Example

- Coherent needles of Si-Mg rich β'' phase play a crucial role in the precipitation hardening of Al-6000 series. How can one estimate the energetics of a growing precipitate?
- Let's think at all the terms that enter the energy of a needle-like precipitates



Precipitates in Al-6xxx - A Worked Example

- Coherent needles of Si-Mg rich β'' phase play a crucial role in the precipitation hardening of Al-6000 series. How can one estimate the energetics of a growing precipitate?
- Let's think at all the terms that enter the energy of a needle-like precipitates



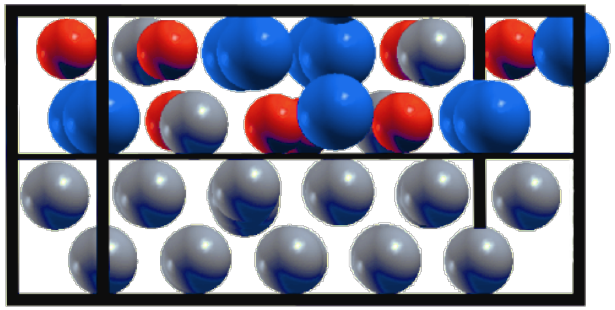
1. Bulk term. Use supersaturated solid solutiong as reference

$$\Delta E_{Mg_5Si_6} = E_{\beta''} + 11Al_{matrix} - 5Mg_{SS} - 6Al_{SS}$$

Precipitates in Al-6xxx - A Worked Example

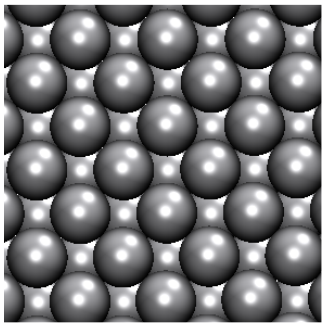
- Coherent needles of Si-Mg rich β'' phase play a crucial role in the precipitation hardening of Al-6000 series. How can one estimate the energetics of a growing precipitate?
- Let's think at all the terms that enter the energy of a needle-like precipitates

surface

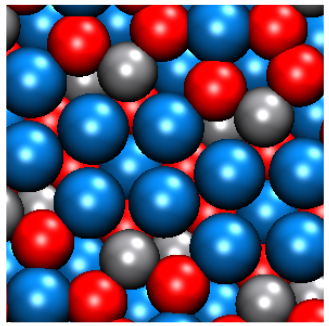


$-N_{Al}$

bulk



$-N_{\beta''}$



2. Surface terms. Compute as a difference between supercells

$$E_{surf} = \left(E_{cell} - N_{Al}E_{Al} - N_{\beta''}E_{\beta''}\right)/A$$

Precipitates in Al-6xxx - A Worked Example

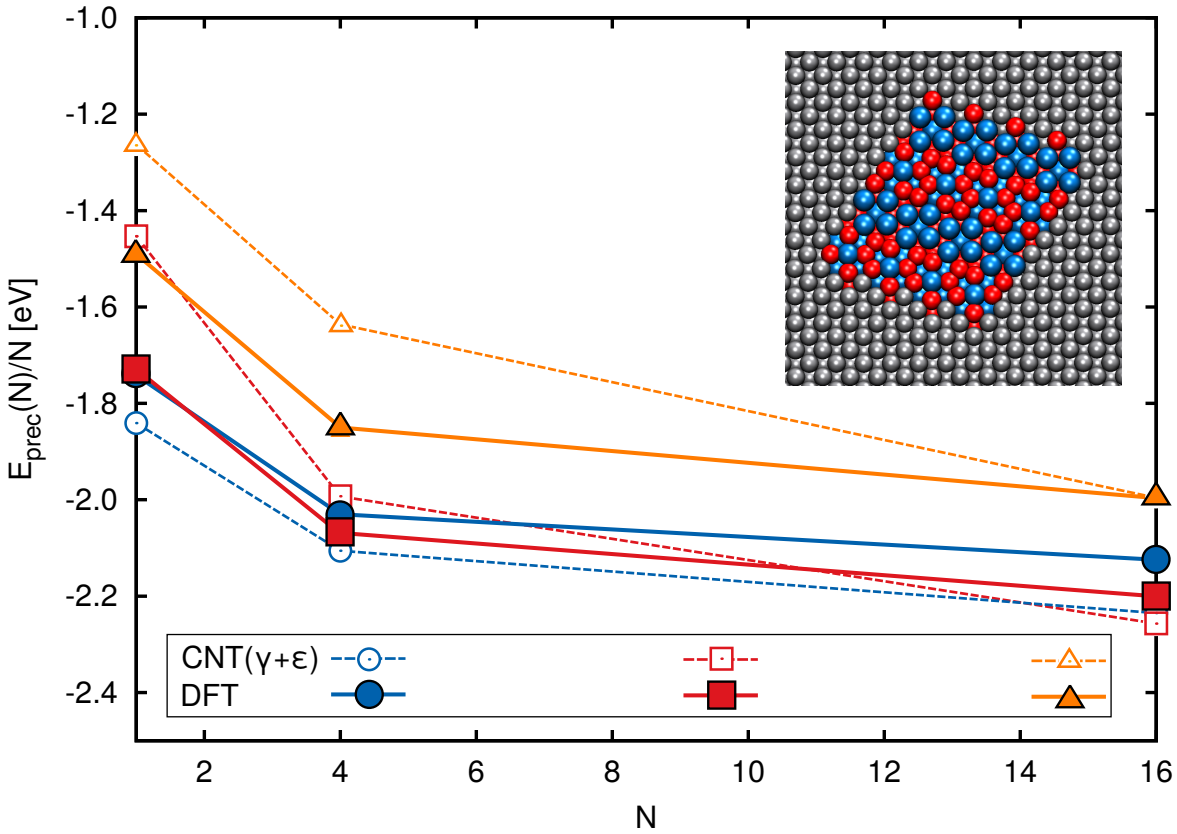
- Coherent needles of Si-Mg rich β'' phase play a crucial role in the precipitation hardening of Al-6000 series. How can one estimate the energetics of a growing precipitate?
- Let's think at all the terms that enter the energy of a needle-like precipitates

Composition	a [Å]	b [Å]	c [Å]	β [°]
Mg_5Si_6	15.14	4.08	6.93	109.9
$Mg_5Al_2Si_4$	15.33	4.05	6.84	106.0
$Mg_4Al_3Si_4$	15.13	4.12	6.65	106.6
Matrix [7]	14.63	4.06	6.41	105.3

3. Non-trivial elastic term due to the slight mismatch in latice parameters

Precipitates in Al-6xxx - A Worked Example

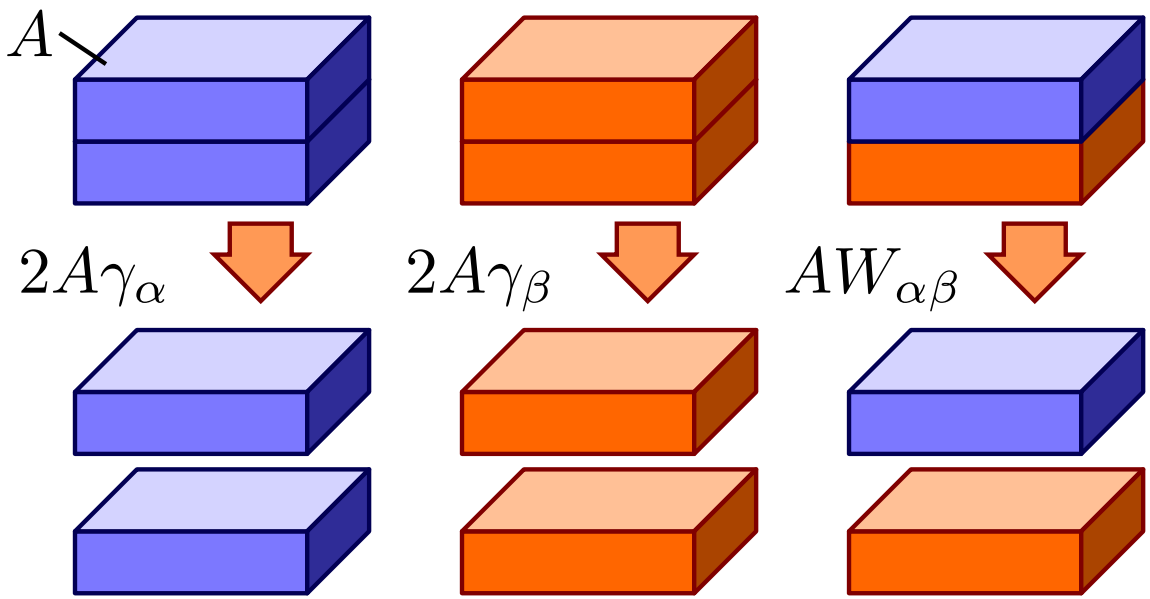
- Coherent needles of Si-Mg rich β'' phase play a crucial role in the precipitation hardening of Al-6000 series. How can one estimate the energetics of a growing precipitate?
- Let's think at all the terms that enter the energy of a needle-like precipitates



4. Check convergence against explicit calculation of finite-size precipitate

Becker Model of Interface Energy

- Remember Young-Dupré equation. Consider two phases α and β, a bond-counting argument, and let x_α and x_β the concentration of the B specie in the two phases

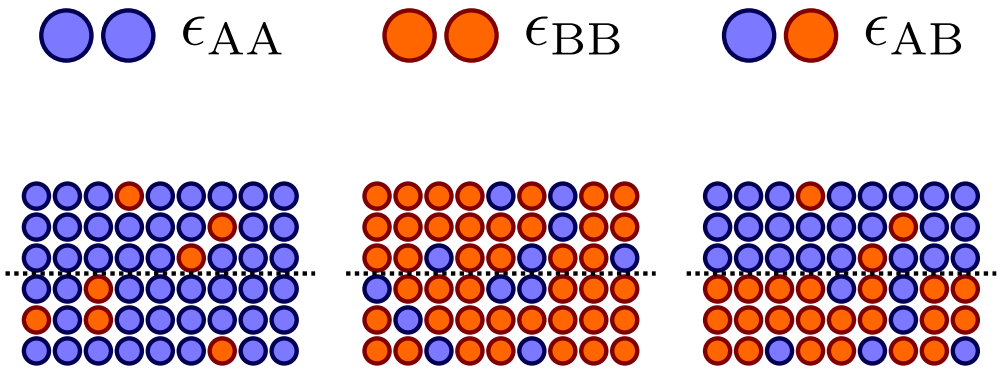


$$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

Becker Model of Interface Energy

- Remember Young-Dupré equation. Consider two phases α and β, a bond-counting argument, and let x_α and x_β the concentration of the B specie in the two phases

$$\frac{2\gamma_\alpha}{Nz} = \epsilon_{BB} x_\alpha^2 + \epsilon_{AA} (1 - x_\alpha)^2 + 2\epsilon_{AB} x_\alpha (1 - x_\alpha)$$

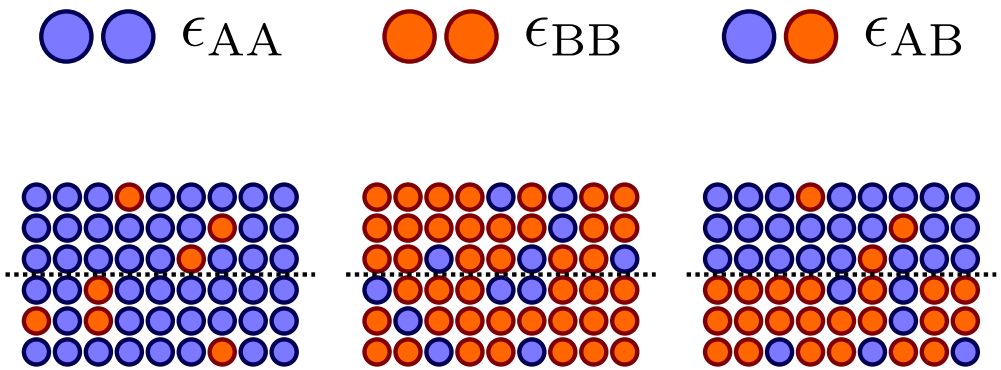


$$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

Becker Model of Interface Energy

- Remember Young-Dupré equation. Consider two phases α and β, a bond-counting argument, and let x_α and x_β the concentration of the B specie in the two phases

$$\frac{2\gamma_\beta}{Nz} = \epsilon_{BB} x_\beta^2 + \epsilon_{AA} (1 - x_\beta)^2 + 2\epsilon_{AB} x_\beta (1 - x_\beta)$$

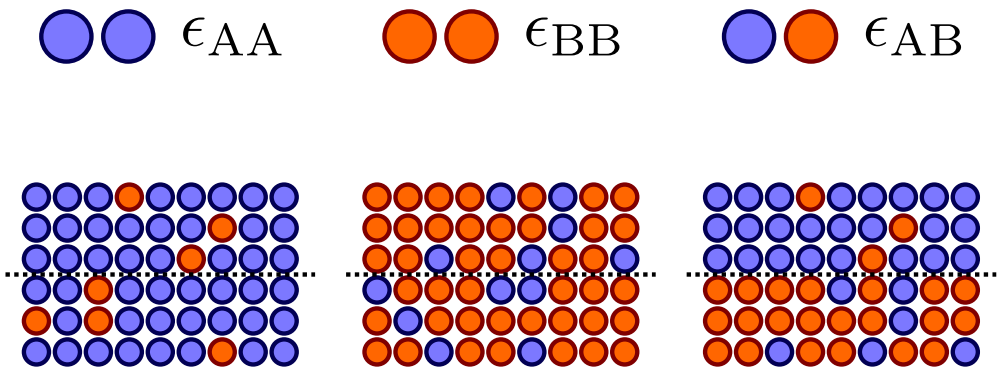


$$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

Becker Model of Interface Energy

- Remember Young-Dupré equation. Consider two phases α and β, a bond-counting argument, and let x_α and x_β the concentration of the B specie in the two phases

$$\frac{W_{\alpha\beta}}{Nz} = \epsilon_{\mathrm{BB}} x_\beta x_\alpha + \epsilon_{\mathrm{AA}} (1 - x_\beta)(1 - x_\alpha) + \epsilon_{\mathrm{AB}} [x_\beta (1 - x_\alpha) + x_\alpha (1 - x_\beta)]$$

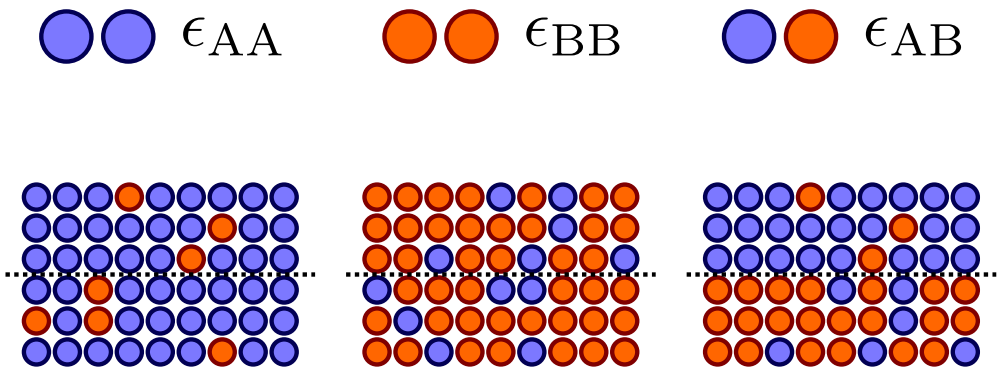


$$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

Becker Model of Interface Energy

- Remember Young-Dupré equation. Consider two phases α and β, a bond-counting argument, and let x_α and x_β the concentration of the B specie in the two phases

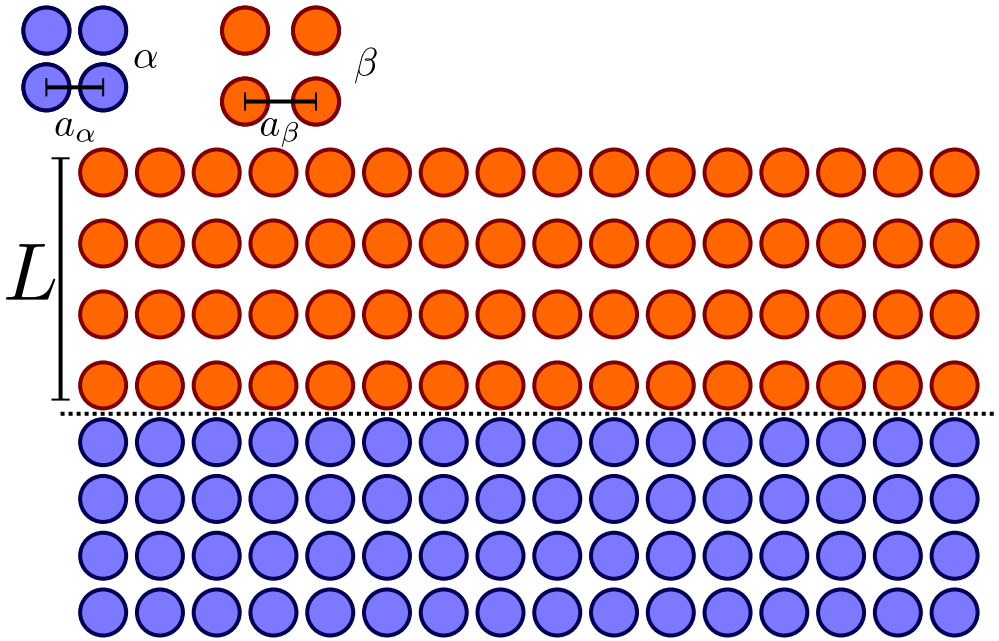
$$\gamma_{\alpha\beta} = Nz\left(\frac{\epsilon_{AA}+\epsilon_{BB}}{2}-\epsilon_{AB}\right)(x_\alpha - x_\beta)^2$$



$$\gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta}$$

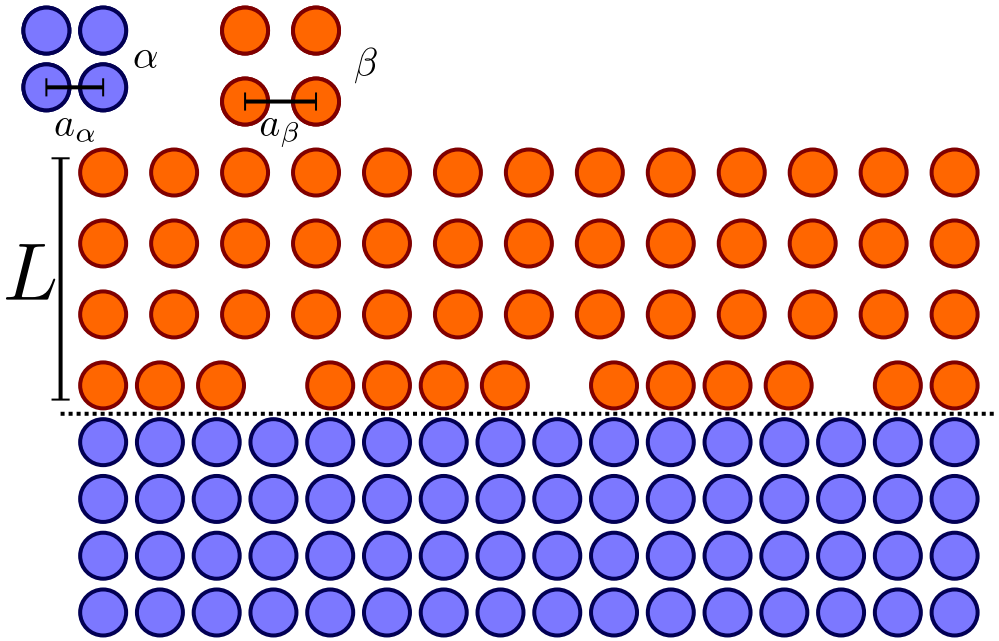
Semi-Coherent Interfaces

- Interface between materials with different lattice pars. a_α and a_β.
  - β might grow epitaxially taking the same lattice parameter of α
  - . . . or it may grow with its own lattice parameter, accommodating the mismatch *with misfit dislocations*
  - Distance between the dislocations must bring the lattices in register
  - . . . best expressed in terms of the dislocation Burger's vector $\bar{b}$, and the lattice misfit $\delta \equiv (a_\beta - a_\alpha) / \bar{b}$



Semi-Coherent Interfaces

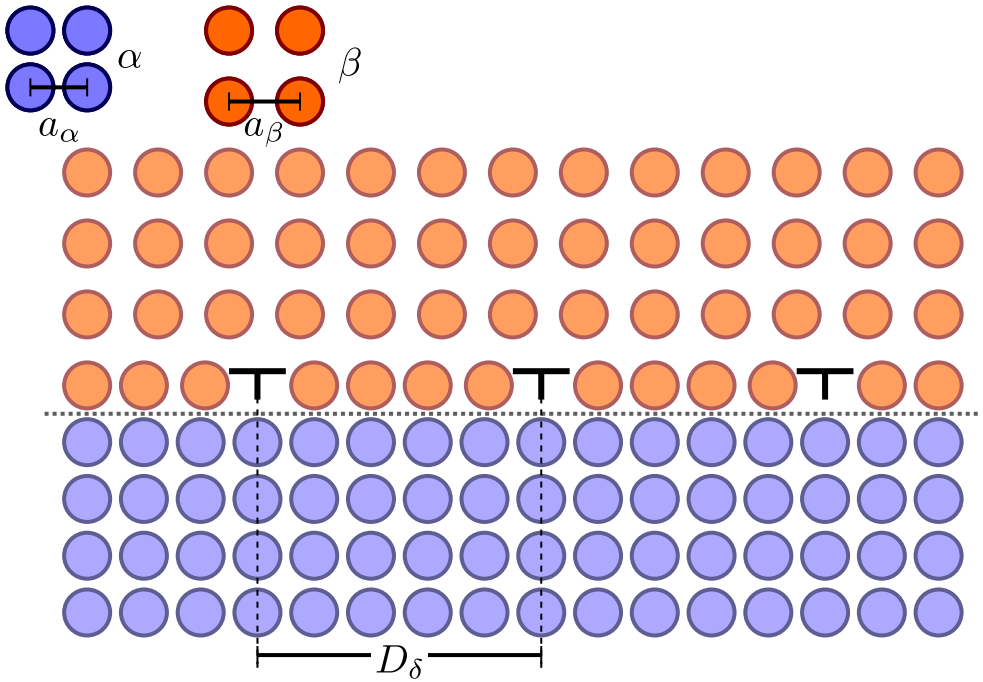
- Interface between materials with different lattice pars. a_α and a_β.
  - β might grow epitaxially taking the same lattice parameter of α
  - . . . or it may grow with its own lattice parameter, accommodating the mismatch *with misfit dislocations*
  - Distance between the dislocations must bring the lattices in register
  - . . . best expressed in terms of the dislocation Burger's vector $\bar{b}$, and the lattice misfit $\delta \equiv (a_\beta - a_\alpha) / \bar{b}$



Semi-Coherent Interfaces

- Interface between materials with different lattice pars. a_α and a_β.
  - β might grow epitaxially taking the same lattice parameter of α
  - . . . or it may grow with its own lattice parameter, accommodating the mismatch *with misfit dislocations*
  - Distance between the dislocations must bring the lattices in register
  - . . . best expressed in terms of the dislocation Burger's vector $\bar{b}$, and the lattice misfit $\delta \equiv (a_\beta - a_\alpha)/\bar{b}$

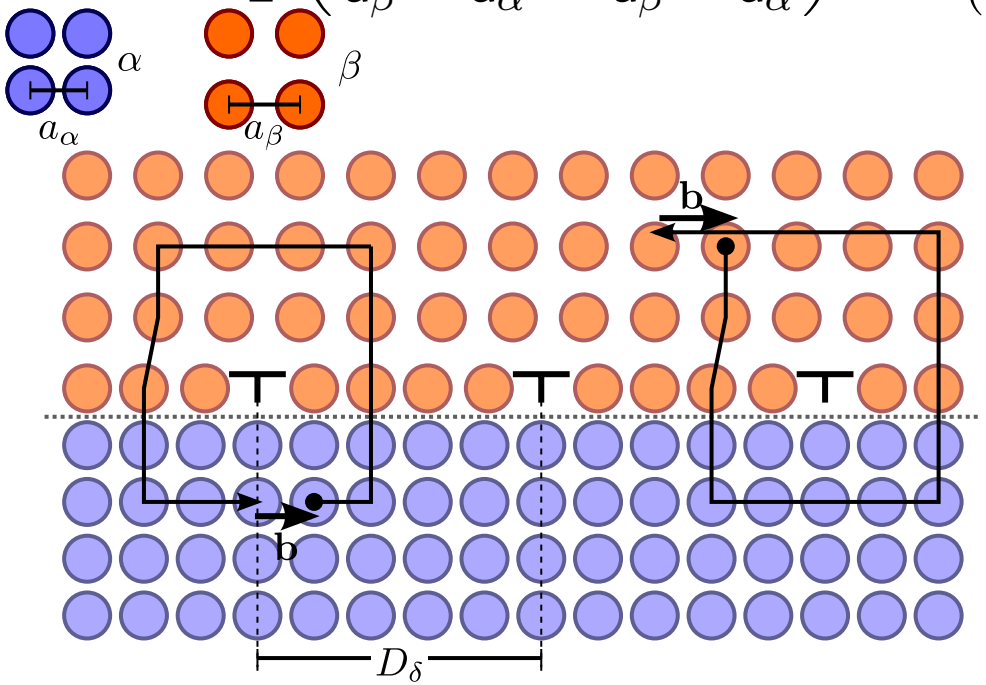
$$D_\delta = n a_\beta = (n+1)\, a_\alpha \;\rightarrow n = \frac{a_\alpha}{a_\beta - a_\alpha}$$



Semi-Coherent Interfaces

- Interface between materials with different lattice pars. a_α and a_β.
  - β might grow epitaxially taking the same lattice parameter of α
  - . . . or it may grow with its own lattice parameter, accommodating the mismatch *with misfit dislocations*
  - Distance between the dislocations must bring the lattices in register
  - . . . best expressed in terms of the dislocation Burger's vector $\bar{b}$, and the lattice misfit $\delta \equiv (a_\beta - a_\alpha)/\bar{b}$

$$\bar{b} = \frac{a_\alpha + a_\beta}{2}, \quad D_\delta \approx \frac{1}{2}\left(\frac{a_\alpha}{a_\beta - a_\alpha} + \frac{a_\beta}{a_\beta - a_\alpha}\right)\bar{b} = \frac{\bar{b}^2}{(a_\beta - a_\alpha)} = \frac{\bar{b}}{\delta}$$

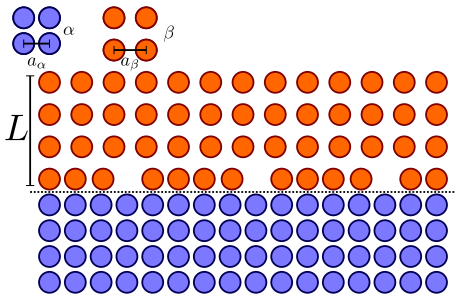


Energy of a Thin Film

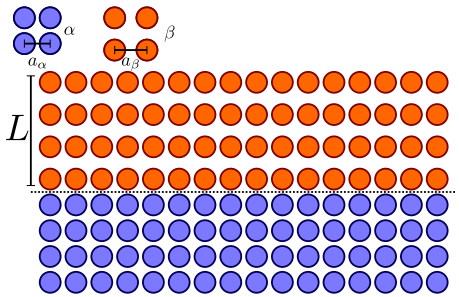
- Elastic energy associated with the dislocation array (μ is the shear modulus, ν is the Poisson ratio) is very similar to the Read-Shockley model of symmetric tilt grain boundaries

$$\gamma_\delta = E_\delta \frac{1}{D_\delta} = E_\delta \frac{\delta}{\bar{b}} \approx \frac{\delta}{2} E_0 \left(A_0 - \ln \delta\right), \qquad E_0 = \frac{\mu \bar{b}}{2\pi \left(1 - \nu\right)}$$

- Elastic energy of a strained epitaxial layer of thickness L.
  - The 1D strain is $\epsilon = \left(a_\beta - a_\alpha\right)/a_\beta$. For small misfits $\epsilon \approx \delta$. The elastic energy is (ignoring many terms, see Howe chapter 14 for more detailed discussion) $\gamma_{\text{epi}} \approx C\delta^2 L$
  - The epitaxial layer and the relaxed layer have the same energy for critical thickness and misfit



$L/\bar{b} > k/\delta_c$



$L/\bar{b} < k/\delta_c$

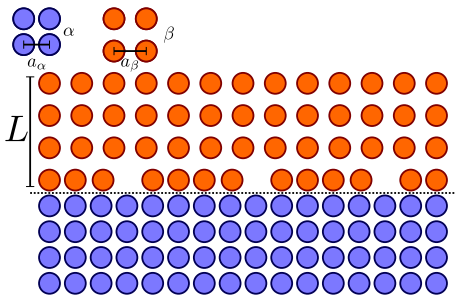
Energy of a Thin Film

- Elastic energy associated with the dislocation array (μ is the shear modulus, ν is the Poisson ratio) is very similar to the Read-Shockley model of symmetric tilt grain boundaries

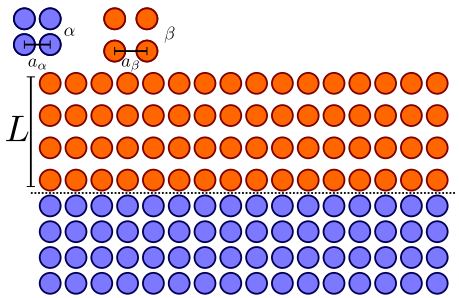
$$\gamma_\delta = E_\delta \frac{1}{D_\delta} = E_\delta \frac{\delta}{\bar{b}} \approx \frac{\delta}{2} E_0 \left(A_0 - \ln \delta\right), \qquad E_0 = \frac{\mu \bar{b}}{2\pi \left(1-\nu\right)}$$

- Elastic energy of a strained epitaxial layer of thickness L.
  - The 1D strain is $\epsilon = \left(a_\beta - a_\alpha\right)/a_\beta$. For small misfits $\epsilon \approx \delta$. The elastic energy is (ignoring many terms, see Howe chapter 14 for more detailed discussion) $\gamma_{\text{epi}} \approx C\delta^2 L$
  - The epitaxial layer and the relaxed layer have the same energy for critical thickness and misfit

$$\gamma_\delta \approx \gamma_{\text{epi}} \rightarrow C\delta^2 L \approx E_\delta \frac{\delta}{\bar{b}}$$



$L/\bar{b} > k/\delta_c$



$L/\bar{b} < k/\delta_c$

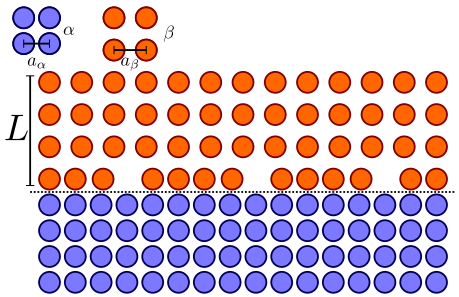
Energy of a Thin Film

- Elastic energy associated with the dislocation array (μ is the shear modulus, ν is the Poisson ratio) is very similar to the Read-Shockley model of symmetric tilt grain boundaries

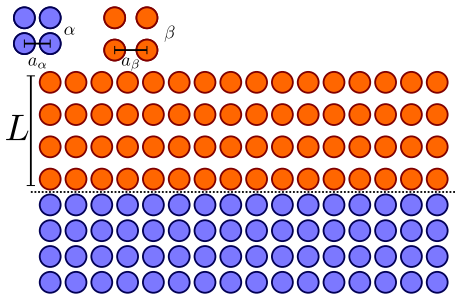
$$\gamma_\delta = E_\delta \frac{1}{D_\delta} = E_\delta \frac{\delta}{\bar{b}} \approx \frac{\delta}{2} E_0 \left(A_0 - \ln \delta\right), \qquad E_0 = \frac{\mu \bar{b}}{2\pi \left(1-\nu\right)}$$

- Elastic energy of a strained epitaxial layer of thickness L.
  - The 1D strain is $\epsilon = \left(a_\beta - a_\alpha\right)/a_\beta$. For small misfits $\epsilon \approx \delta$. The elastic energy is (ignoring many terms, see Howe chapter 14 for more detailed discussion) $\gamma_{\text{epi}} \approx C\delta^2 L$
  - The epitaxial layer and the relaxed layer have the same energy for critical thickness and misfit

$$\frac{L_c}{\bar{b}} \approx \frac{E_\delta}{C\bar{b}^2} \frac{1}{\delta_c} \approx \frac{\left(A_0 - \ln \delta_c\right) E_0/2}{C\bar{b}} \frac{1}{\delta_c} = \frac{1}{\delta_c} \frac{\mu/C}{4\pi\left(1-\nu\right)} \left(A_0 - \ln \delta_c\right)$$



$L/\bar{b} > k/\delta_c$



$L/\bar{b} < k/\delta_c$

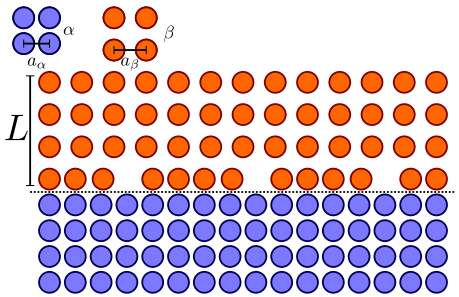
Energy of a Thin Film

- Elastic energy associated with the dislocation array (μ is the shear modulus, ν is the Poisson ratio) is very similar to the Read-Shockley model of symmetric tilt grain boundaries

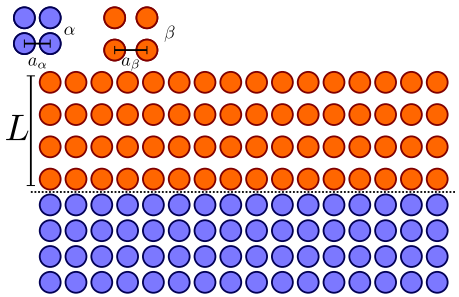
$$\gamma_\delta = E_\delta \frac{1}{D_\delta} = E_\delta \frac{\delta}{\bar{b}} \approx \frac{\delta}{2} E_0 \left(A_0 - \ln \delta\right), \qquad E_0 = \frac{\mu \bar{b}}{2\pi \left(1-\nu\right)}$$

- Elastic energy of a strained epitaxial layer of thickness L.
  - The 1D strain is $\epsilon = \left(a_\beta - a_\alpha\right)/a_\beta$. For small misfits $\epsilon \approx \delta$. The elastic energy is (ignoring many terms, see Howe chapter 14 for more detailed discussion) $\gamma_{\text{epi}} \approx C\delta^2 L$
  - The epitaxial layer and the relaxed layer have the same energy for critical thickness and misfit

$$\frac{L_c}{\bar{b}} \approx \frac{E_\delta}{C\bar{b}^2} \frac{1}{\delta_c} \approx \frac{\left(A_0 - \ln \delta_c\right) E_0/2}{C\bar{b}} \frac{1}{\delta_c} = \frac{1}{\delta_c} \frac{\mu/C}{4\pi\left(1-\nu\right)} \left(A_0 - \ln \delta_c\right)$$



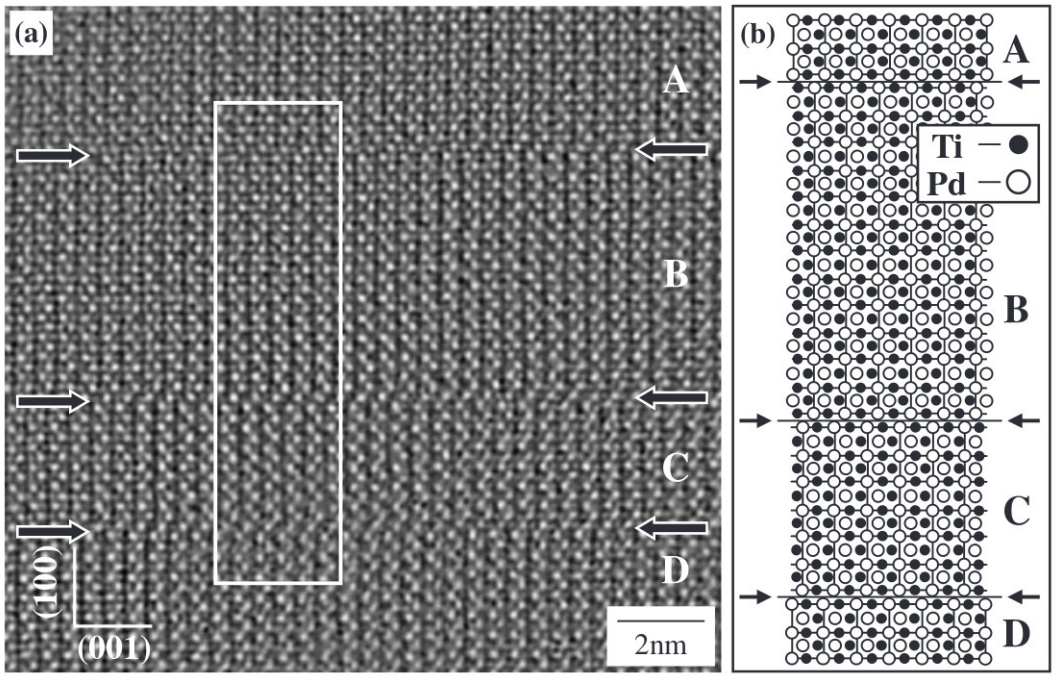
$L/\bar{b} > k/\delta_c$



$L/\bar{b} < k/\delta_c$

Antiphase Boundaries

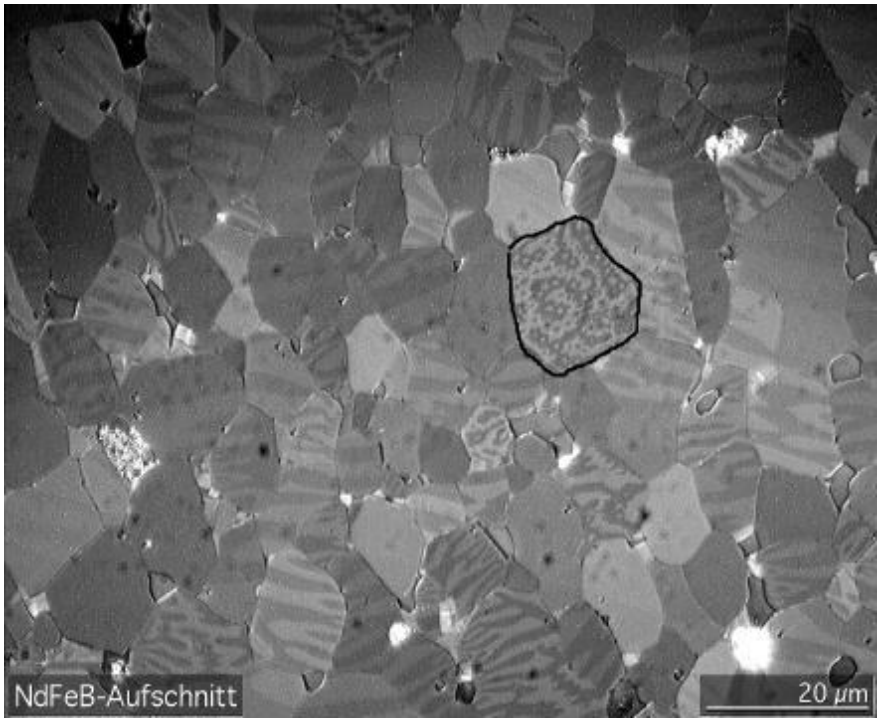
- A special kind of heterophase grain boundary is given by **antiphase boundaries**. The two grains have the same material and crystal structure, but a different ordering.
- Close relatives of twin boundaries
- The two regions can have the same structure but different magnetic or electronic properties (**domains** in magnetic or ferroelectric materials)



Antiphase-like boundaries in Ti-Pd shape-memory alloys. [Matsuda et al., Mat. Transac., 2008]

Antiphase Boundaries

- A special kind of heterophase grain boundary is given by **antiphase boundaries**. The two grains have the same material and crystal structure, but a different ordering.
- Close relatives of twin boundaries
- The two regions can have the same structure but different magnetic or electronic properties (**domains** in magnetic or ferroelectric materials)



Magnetic domains of opposite orientation are seen within each grain in a NdFeB magnet