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Ab-initio study of Co_2MnSi(001) surface and Co_2MnSi/GaAs(001) interface

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Ab initio study of $Co_2MnSi(001)$ surface and $Co_2MnSi/GaAs(001)$ interface

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Outline

- ✓ Spintronics and Half metals
- ✓ A brief review of the surface properties of Co2MnSi(001)
- ✓ Co_2MnSi/GaAs(001) interfaces
- ✓ Thermodynamic study of interfaces (phase diagram)
- ✓ Spin resolved DOS in the interface region
- ✓ Effect of Mn segregation to the interface
- ✓ Magnetic properties

Spintronics

Spintronics = spin based electronics

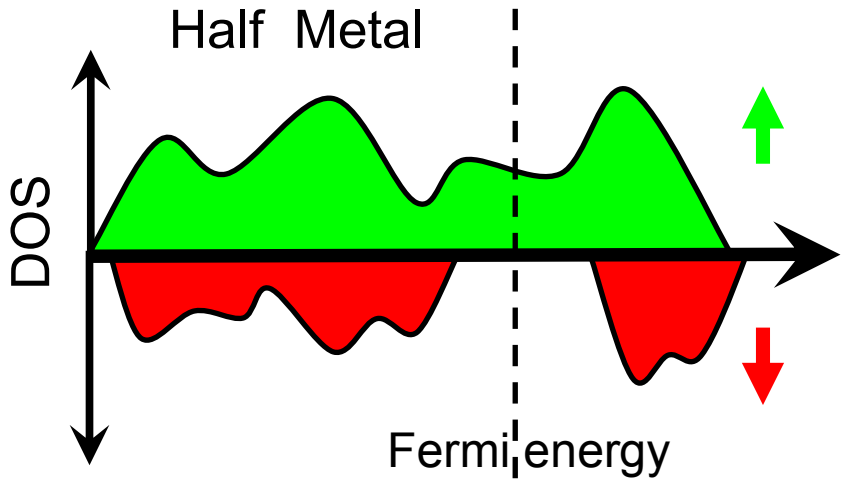
Spin degree of freedom is added to the system

Magnetism ← Spintronics → Electronics

Spin injection an attractive issue in spintronic:

For efficient spin injection new ferromagnets with high spin polarization are required.

Half metals



$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} = 100\ \%$$

promising materials for spin injection application

Co2MnSi is an attractive half metal:

- Highest Curie temperature among all Heusler alloys (985K)
- Wide gap in the minority spin channel

A general approach in spintronic

spintronic devices  semiconductor technology

- Magnetic RAM (nonvolatile, fast, small, low power
- Magnetic field sensors
- Read heads for hard drives (more sensitive)

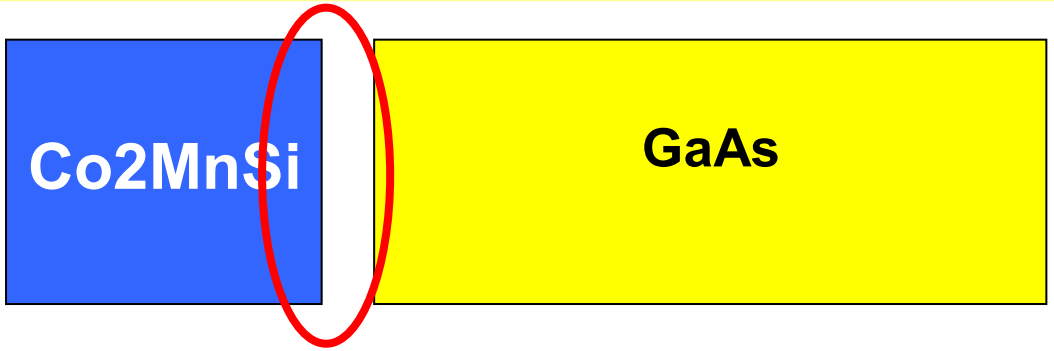
separated from MOSFET technology

An attractive issue in spintronic

Epitaxial growth of a half metal on a semiconductor substrate:

Is the half metallicity saved at the interface?

Interface of Co2MnSi and GaAs



Co2MnSi is a promising material for Spintronics (Spin injector)

GaAs is a well-known semiconductor with similar structure

More about Co2MnSi

More attractive properties:

- Structural similarity with GaAs
- Low lattice mismatch

Experimental lattice constants (Å)

Co_2MnSi		GaAs
5.67		5.65

Measured spin polarizations

- Bulk Co2MnSi P=50-60% [1]
- Co2MnSi film on GaAs(001) P=12% [2]
- Co2MnSi film on GaAs(001) $P_{\text{free surface}}$=55% [3]

$$P_{\text{theo}}\,(\text{bulk}) = 100\%$$

[1] L. Ritche et al. PRB 78 , 104430 (2003)

[2] wang et al, PRB 71, 144416 (2005)

[3] L. J Singh et al, J, Appl. Phys 99, 013904 (2006)

Procedure of the talk

- A brief review of the surface properties of Co2MnSi(001)
- More details on the interface

Computational approach

quantum mechanical approach
within density functional theory

Interface calculations were done by:

ESPRESSO Package

PWscf (Plane-Wave pseudopotential Self Consistent Field)

(http:// www. Pwscf .org)

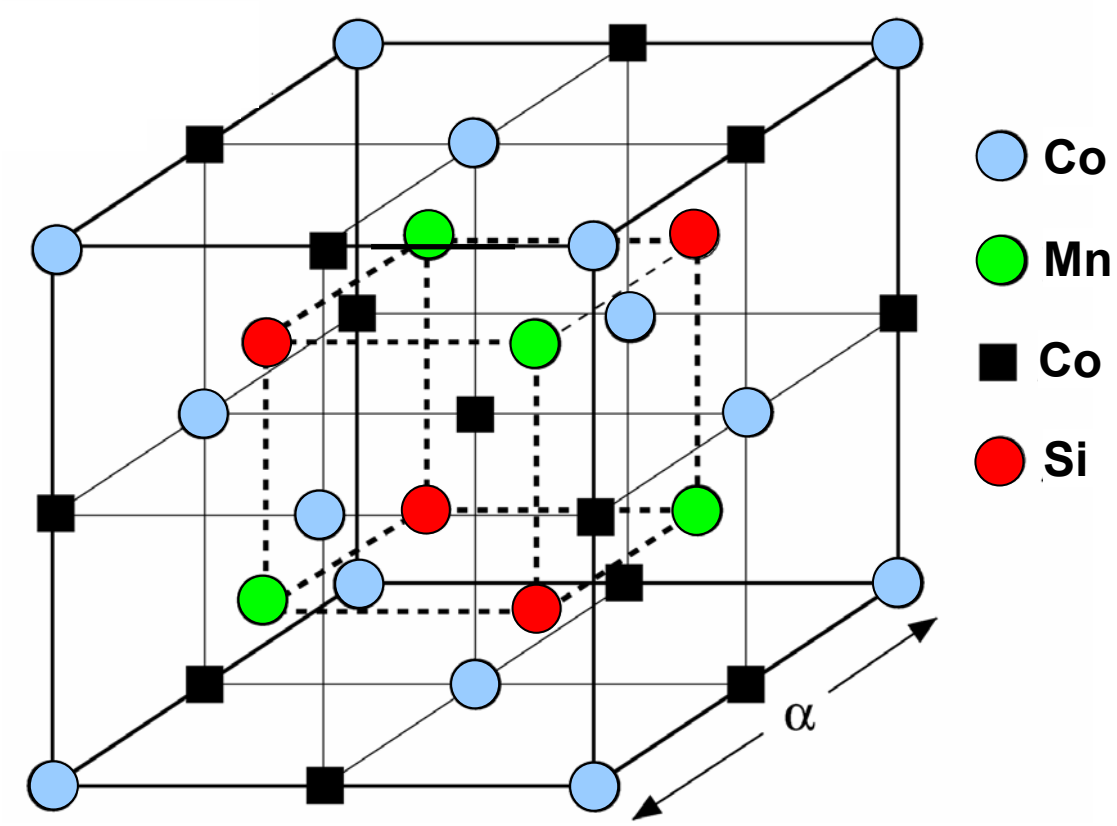
Surface calculations were done by:

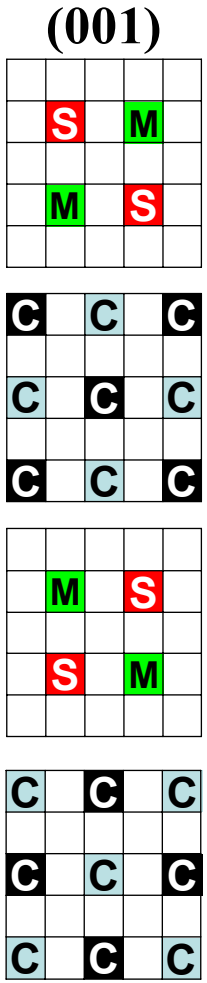
Wien2k (www.wien2k.at)

– Full Potential Linearized Augmented Plane Wave method

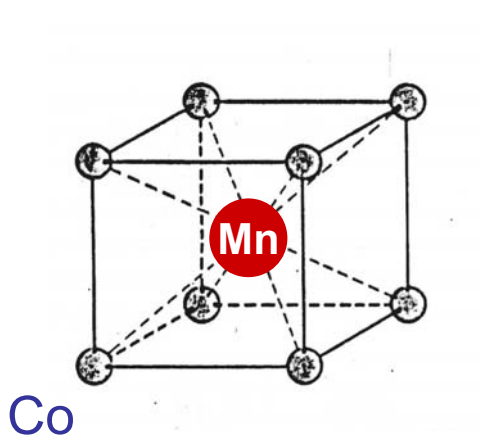
Structure of Co2MnSi

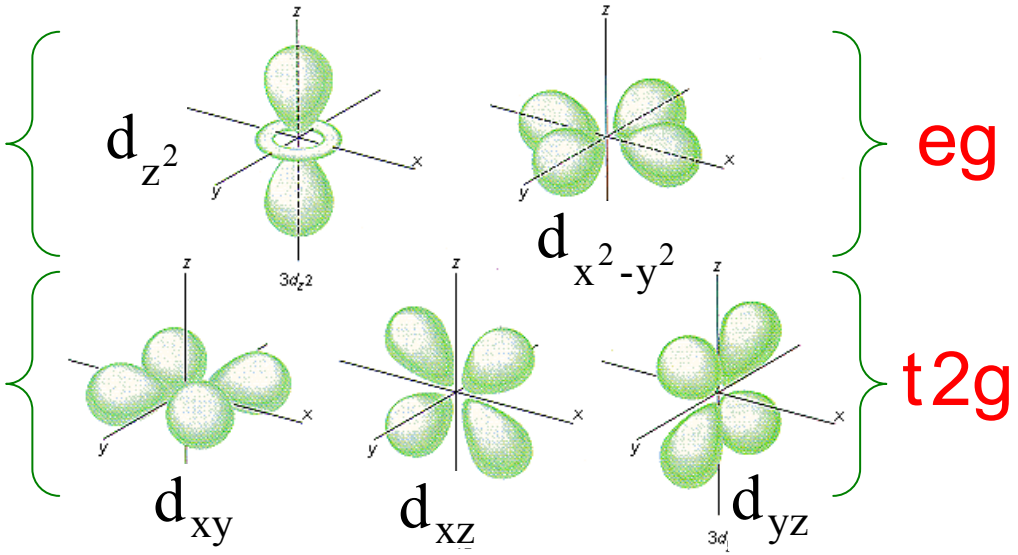
$L2_1$ structure, Four FCC sublattice





bulk Co_2MnSi





Mn atoms are located at the center of the cubes of Cobalt

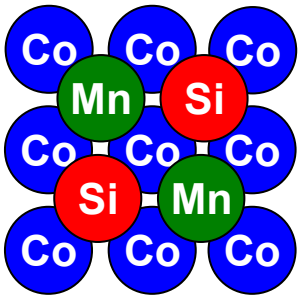
More overlap between t2g orbitals than eg orbitals

Co-Mn bond is mainly via t2g channel

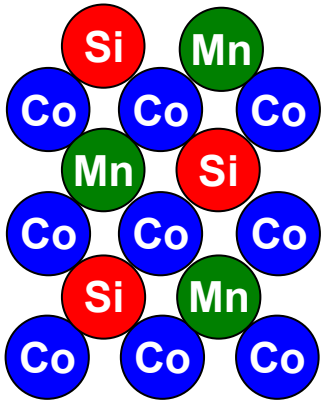
Co_2MnSi (001) ideal Surfaces

MnSi/CoCo Surface

Top view



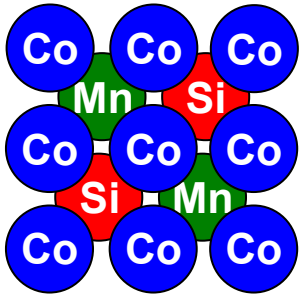
Side view



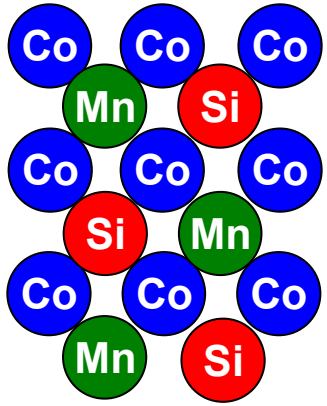
Bulk

CoCo/MnSi Surface

Top view

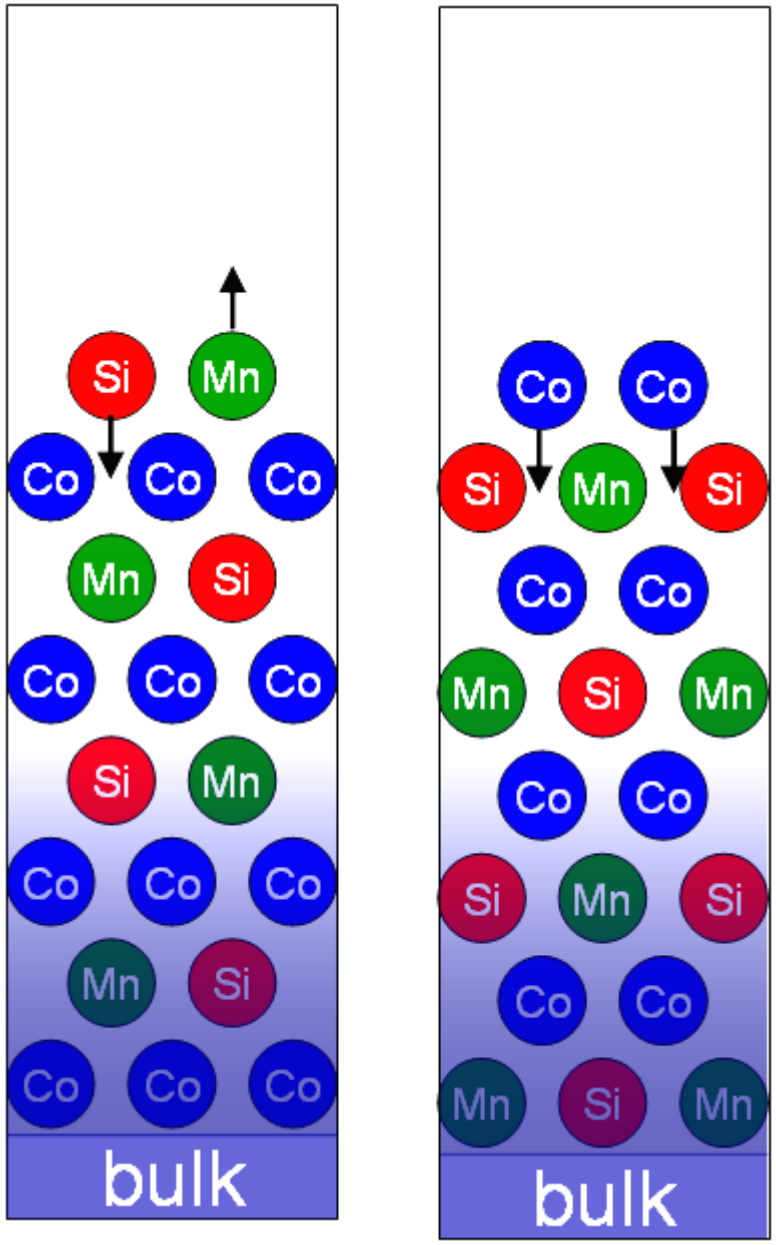


Side view



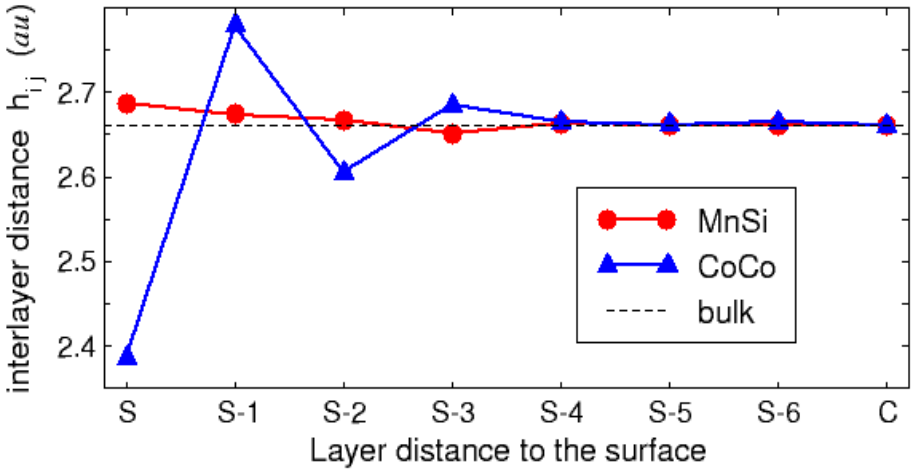
Bulk

Atomic relaxation



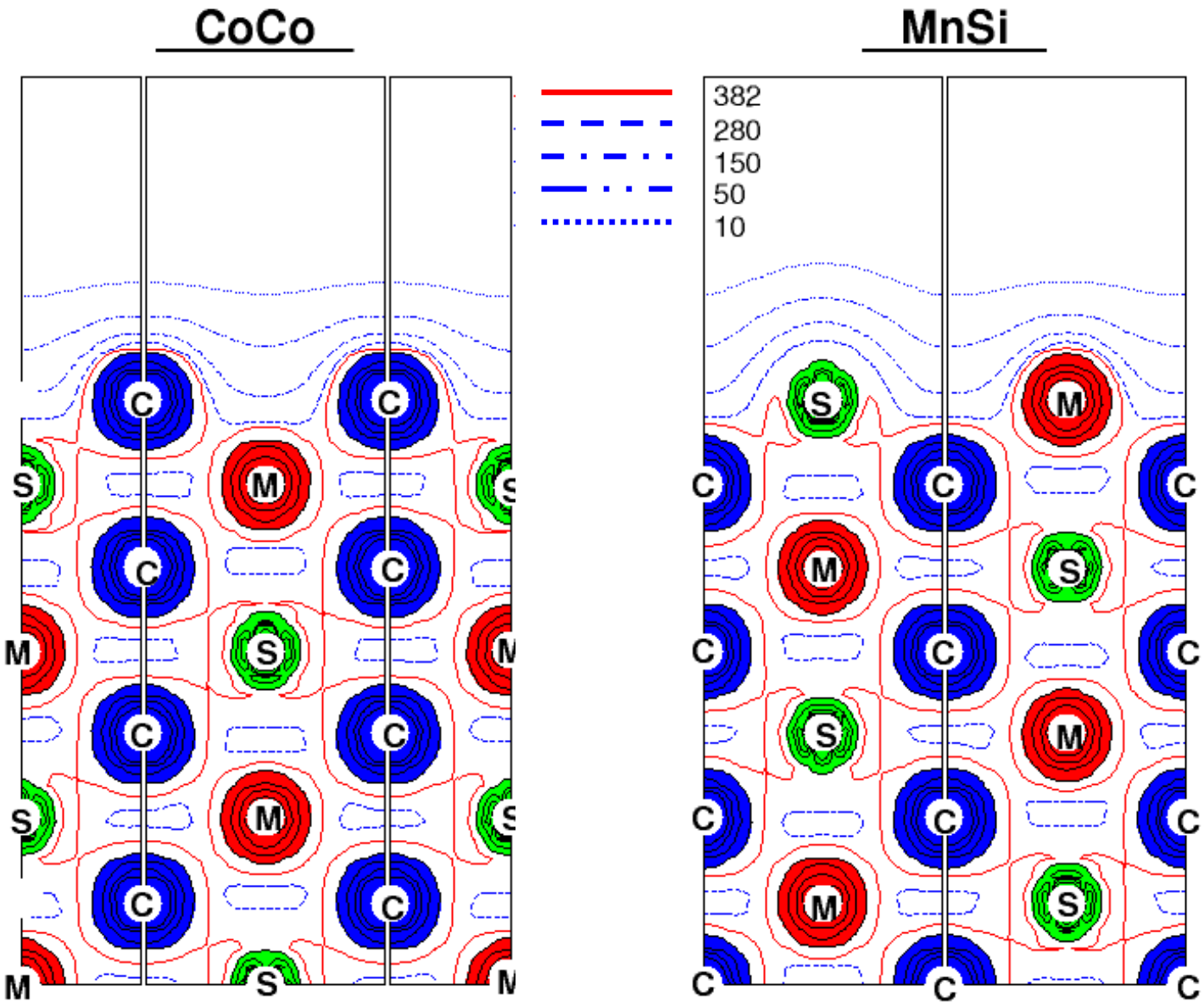
Co-Si bond is stronger than Co-Mn bond

Surface buckling of MnSi=0.55 au



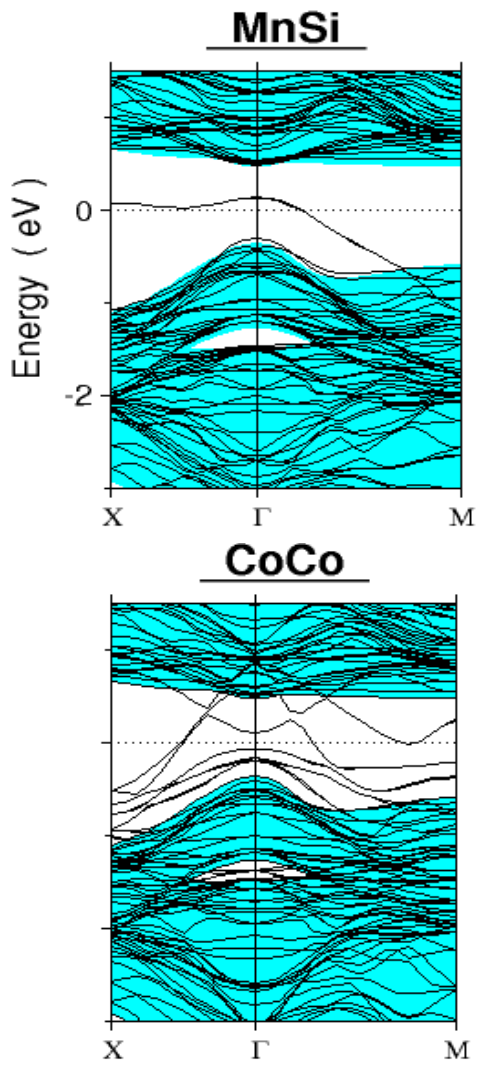
Surface Freidel oscillation is more visible in CoCo surface

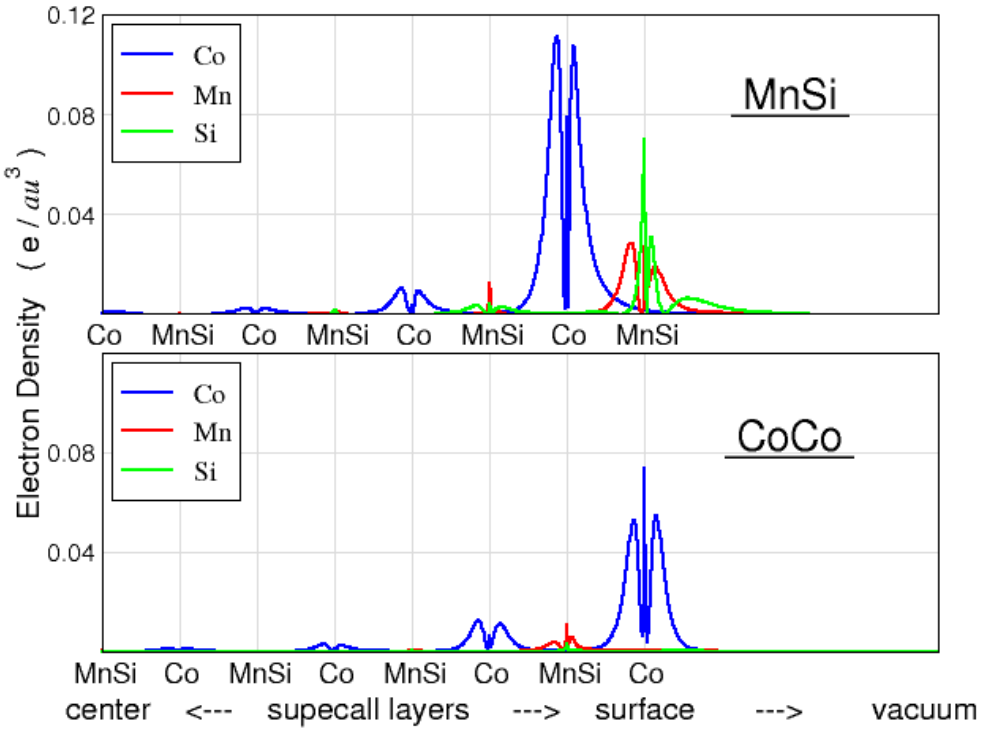
Difference electron density along (110)



ideal terminations – surface states

minority band

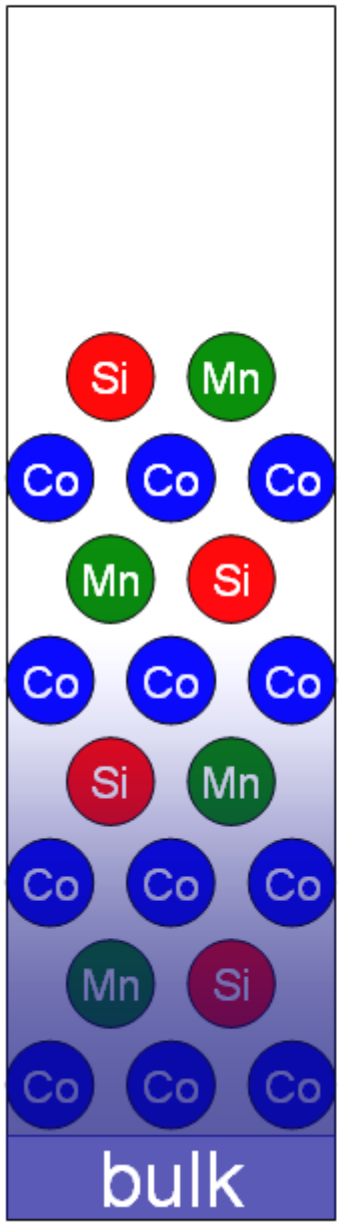




surface states are mainly in the first few layers

surface states of CoCo have higher kinetic energy

$Co_2MnSi(001)$ - modified terminations



MnSi

Mn↕Mn↑

Mn↕Mn↓

Si Si

-- Si

CoSi

MnCo

Mn --

CoCo

CoMn

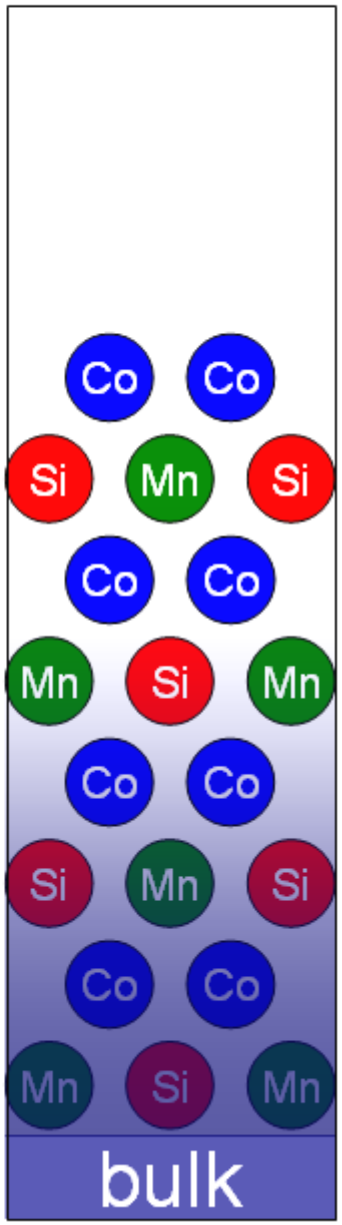
CoSi

Mn↕Mn↑

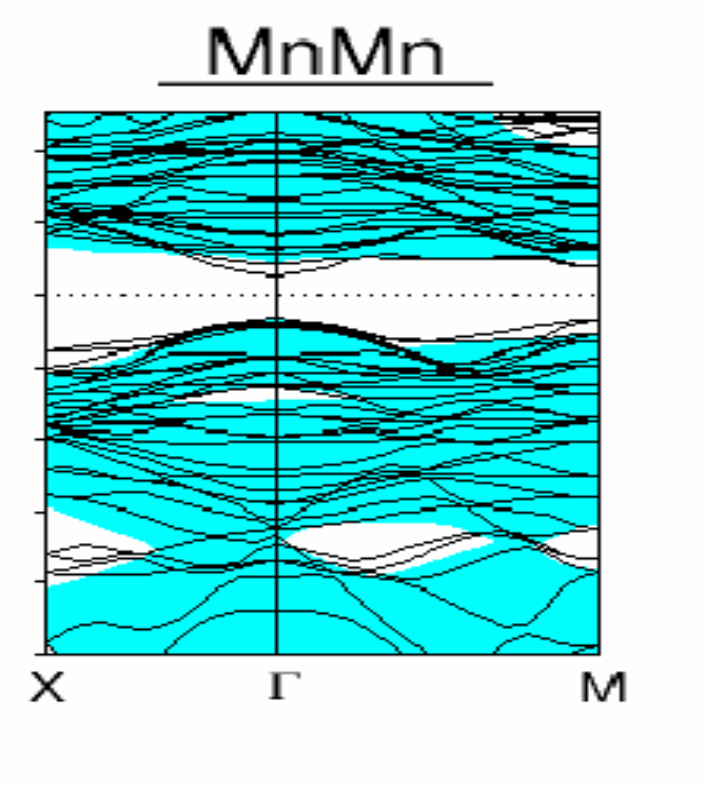
Mn↓Mn↓

Si Si

Co --



Only pure Mn termination preserves the half-metallicity



Covering the $Co_2MnSi(001)$ by a pure Mn layer preserves the half metallicity [1]

[1] Hashemifar, Kratzer, Scheffler, Phys. Rev. Lett. **94** (2005) 096402

Why pure Mn termination preserves the half-metallicity?

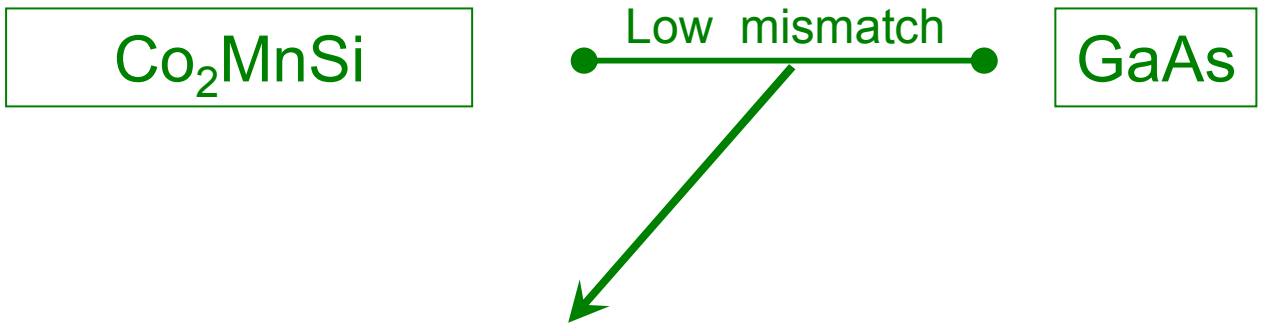
- The origin of Half metallicity in bulk Co2MnSi: Exchange interaction between d electrons of one Mn and two Co atoms [5].
- For MnMn surface, two Mn atom at the surface couple with one Co atom in subsurface.This coupling is probably as strong as interaction between one Mn and two Co in bulk Co2MnSi. Adding one Mn atom in the MnMn surface compensates the deficiency of one Co atom.

[5] I.Galanakis, et.al, Phys. Rev. B66, 174429(2002)

First Conclusion

1. Co-Si bond is stronger than Co-Mn bond and enhances at the surface
2. Surface Freidel oscillation is more visible in CoCo surface compared to MnSi surface.
3. MnSi surface has more surface buckling than CoCo surface.
4. A pure Mn cap layer protects well half-metallicity

Co2MnSi / GaAs(001) interfaces



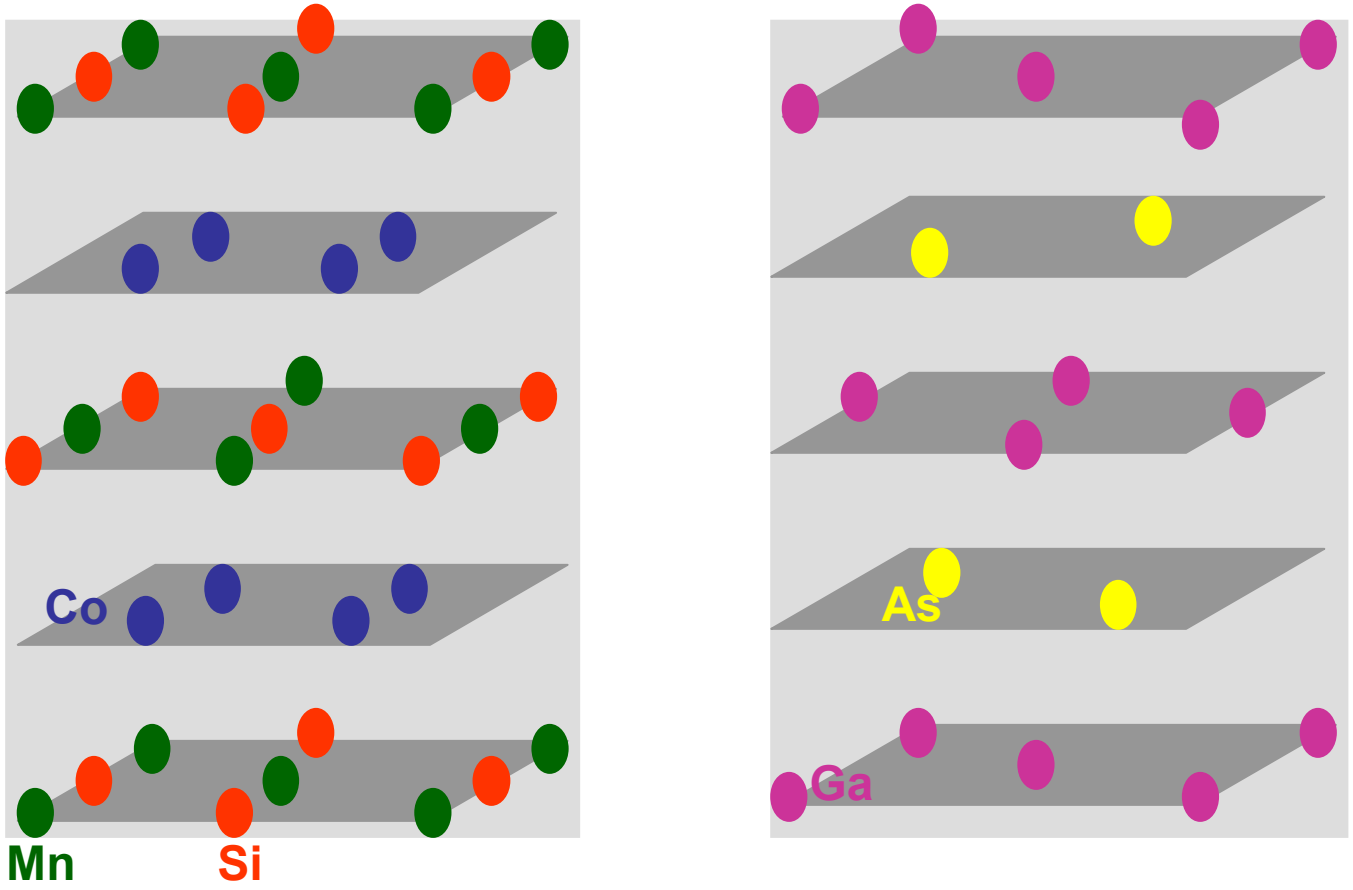
Experimental lattice constants (Å)

Co_2MnSi	GaAs
5.67	5.65

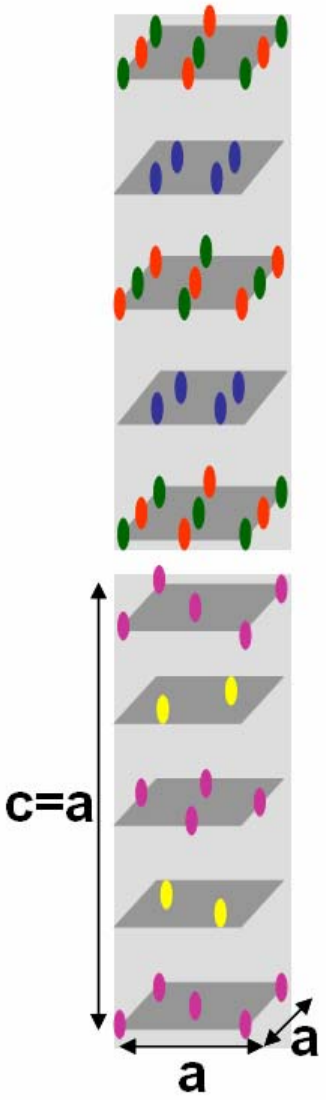
$Co_2MnSi/GaAs(001)$

Co_2MnSi ⟵ fcc ⟶ GaAs

(001) surfaces

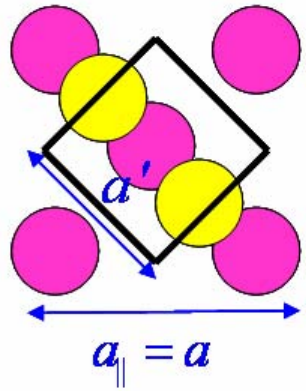


Supercell approach



GaAs

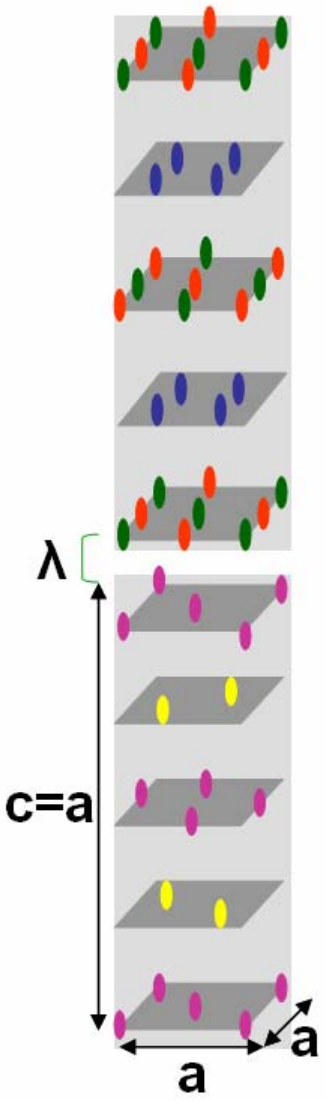
$$\begin{cases} a' = b' = \dfrac{a_{\parallel}}{\sqrt{2}} = \dfrac{a_{GaAs}}{\sqrt{2}} \\ c' = a_{GaAs} \end{cases}$$



Co_2MnSi

$$\begin{cases} a'' = b'' = a' = b' = \dfrac{a_{\parallel}}{\sqrt{2}} = \dfrac{a_{GaAs}}{\sqrt{2}} \\ c'' \rightarrow Optimization \end{cases}$$

Supercell approach



Optimization procedure:

- ✓ Optimize c'' by minimizing the stress along z direction in bulk Co_2MnSi
- ✓ Number of layers :

Initial no. of GaAs layers : 15

& optimize no. of Co_2MnSi layers { 7, 11, 15 / 9, 13

(look at atomic DOS at the center of slab)

- ✓ Distance between two slabs (**λ**) by minimizing the stress along z direction

Which termination?

1- MnSi/Ga

2- MnSi/As

3- CoCo/Ga

4- CoCo/As

✓ Calculate the phase diagram by ab initio thermodynamics

ab initio Thermodynamics

Most stable termination ? "The one with lowest interface formation energy"

How to calculate interface formation energy? "ab-initio Thermodynamics"

$P = 0 \quad T = 0$ —DFT→ **internal energy**

$P > 0 \quad T > 0$ —DFT + thermodynamic = ab initio thermodynamic→ **interface formation energy** [7]

An interface contains two joined surfaces each of them is assumed to be in thermodynamic equilibrium with it's environment (P,T)

Environment ≡ Reservoir

Grand Canonic Ensemble

Appropriate Thermodynamic Free energy : Grand potential

[7] K. Reuter and M. Scheffler, PRB 68 (2001) 035406

interface Formation Energy

interface contribution to the Grand Potential

$$\gamma = \frac{1}{2A}\left[G(T,P) - \sum_i N_i \mu_i\right]$$

i : Co, Mn, Si, Ga, As

interface formation energy

Criteria of Stability

The most stable interface → The one that minimize γ (T,P)

Assume: Interface is in equilibrium with the bulk.

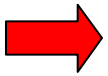
Hence:

Chemical potentials are not completely independent.

Equilibrium with bulk :

$$2\mu_{\mathrm{Co}} + \mu_{\mathrm{Mn}} + \mu_{\mathrm{Si}} = g^{bulk}_{Co_2MnSi}$$

$$\mu_{\mathrm{Ga}} + \mu_{\mathrm{As}} = g^{bulk}_{GaAs}$$



independent chemical potentials (Mn , Co , As)

$$\gamma \approx \frac{1}{2A}\left[G^{slab} - G^{bulk}\right] = \frac{1}{2A}\Delta G$$

$$G = E^{total} + E^{ph} + PV$$

At ambient pressure

$\mathrm{PV} << \mathrm{E}^{\mathrm{total}}$

$$\Rightarrow \gamma \approx \frac{1}{2A}\Delta G = \frac{1}{2A}\left\{ \Delta E^{tot} + \Delta E^{ph} \right\}$$

While phonon free energy is not trivial several authors argue that ΔE^{ph} is considerably lower than ΔE^{tot}

$$\Rightarrow \quad \Delta G \approx \Delta E^{\,tot} \qquad \Rightarrow \qquad \gamma \cong \frac{1}{2A}\left[E^{\,slab} - \sum_i N_i \mu_i \right]$$

Chemical potentials are bounded

μ_{Co} too low → Co leaves the sample → $\mu_{Mn} + \mu_{Si} = g^{bulk}_{MnSi}$
MnSi crystallize at the interface →

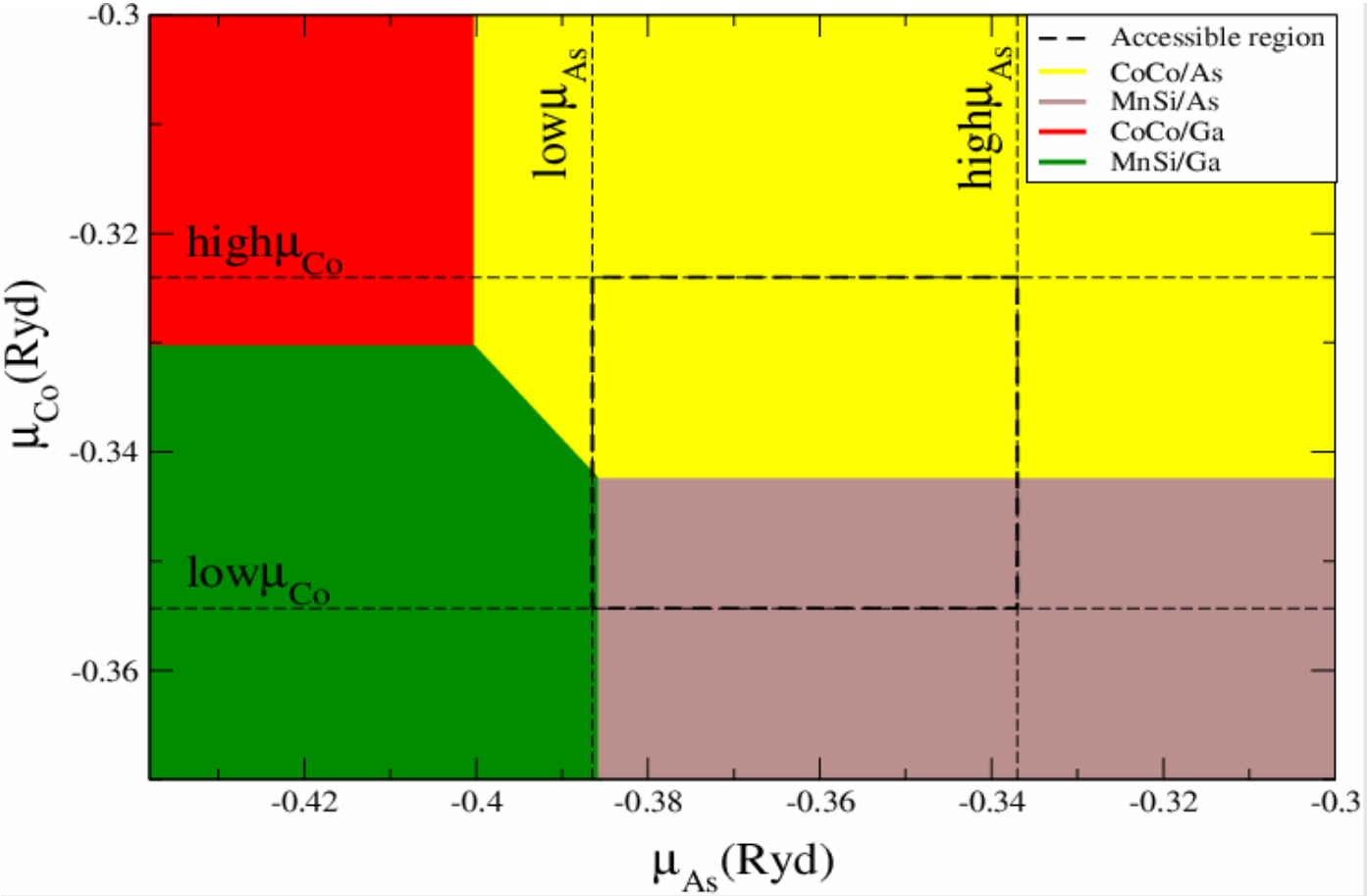
μ_{Co} too high → Co crystallize at the surface → $\mu_{Co} = g^{bulk}_{Co}$

μ_{As} too low → As leaves the sample →
Ga crystallize at the interface →

$$\mu_{Ga} = g^{bulk}_{Ga}$$
$$\mu_{As} = g^{bulk}_{GaAs} - g^{bulk}_{Ga}$$

μ_{As} too high → As crystallize at the surface → $\mu_{As} = g^{bulk}_{As}$

Phase Diagram

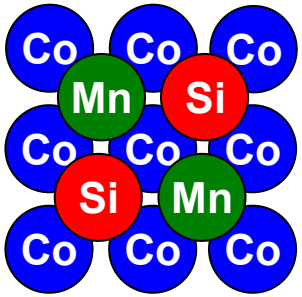


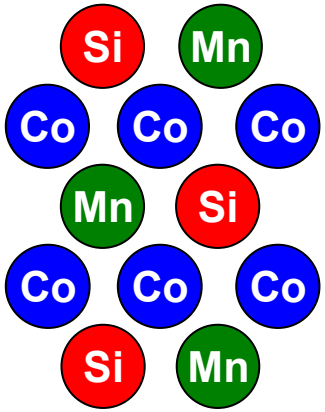
- **MnSi/As and CoCo/As terminations are the most stable interfaces.**
- **Let,s focus on MnSi/As**

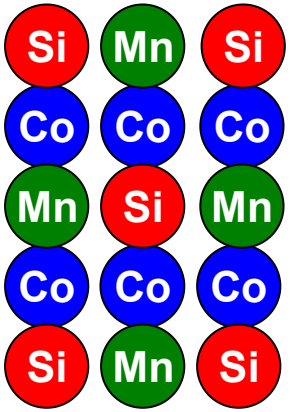
MnSi/As termination

Top view (fcc) **Side view (fcc)** **Side view (tetragonal)**

Co_2MnSi

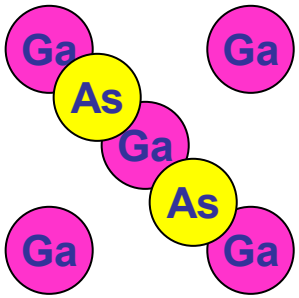


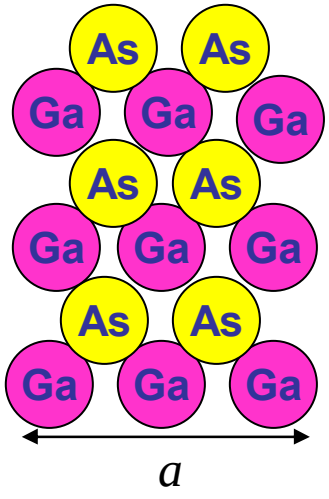


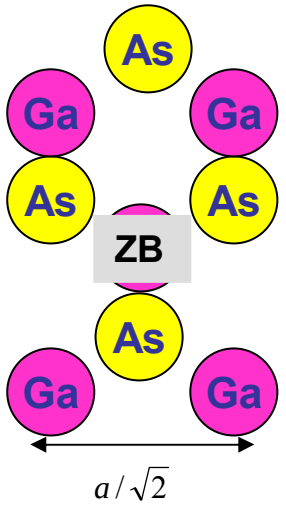


$L2_1$ (Two ZB, CoSi and CoMn)

GaAs







Bulk **Bulk**

MnSi/As termination

Four different morphology

CoMn ZB on GaAs ZB

- **Mn on Ga and**

  Co on As sublattices : Mn(Ga)

- **Mn on As and**

  Co on Ga sublattices : Mn(As)

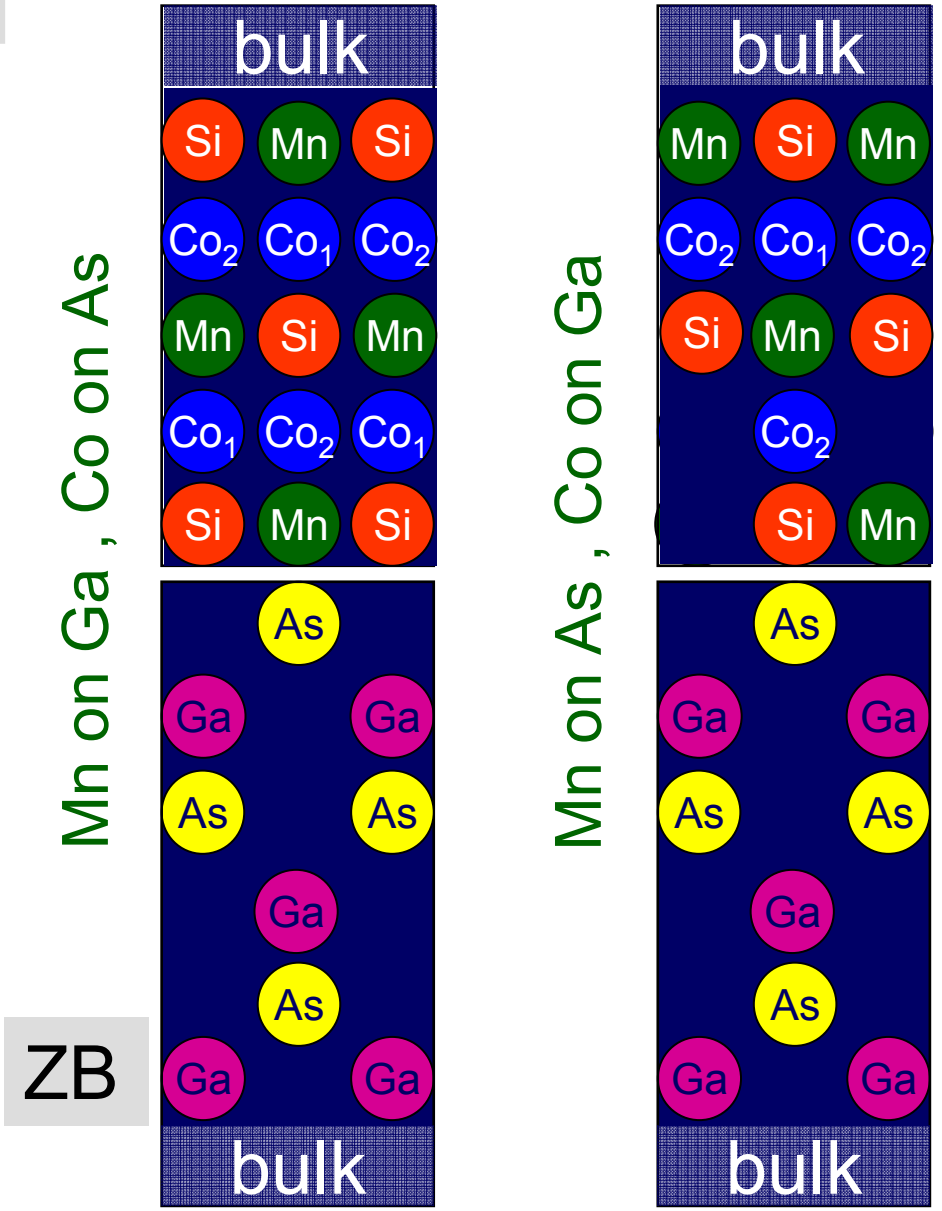
CoSi ZB on GaAs ZB

- **Si on Ga and**

  Co on As sublattices : Si(Ga)

- **Si on As and**

  Co on Ga sublattices : Si(As)



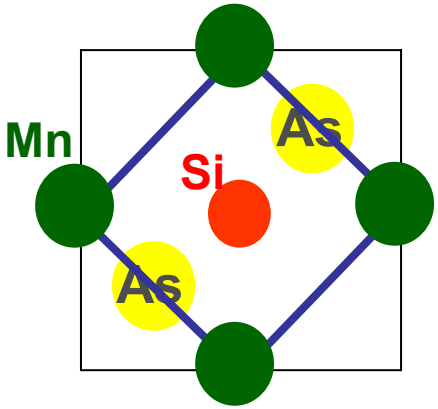
Which morphology (pattern)?

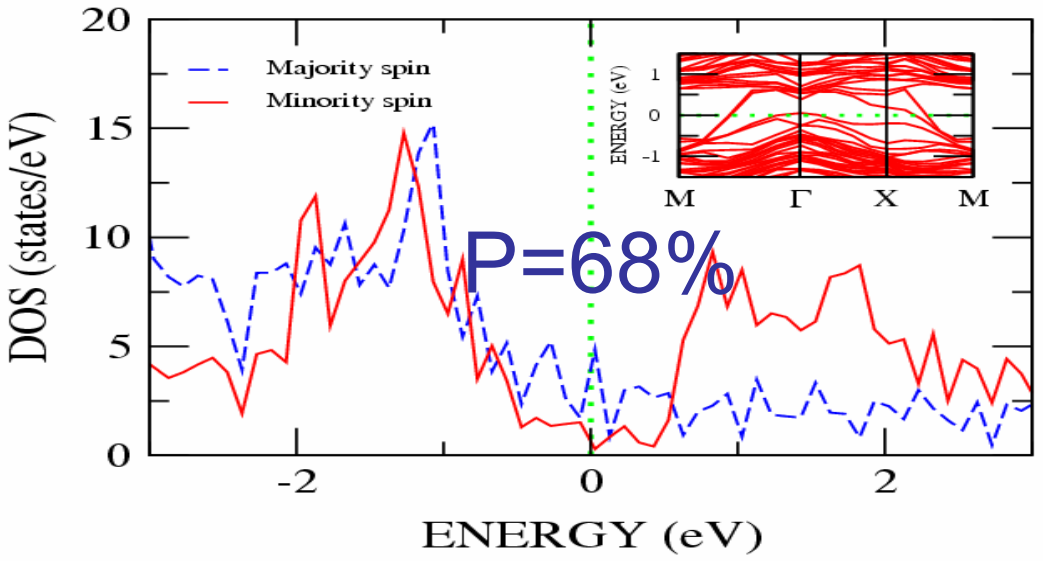
Formation Energy

- Si(Ga) and Si(As) are highly unfavoured
- Mn(Ga) and Mn(As) have a rather small energy difference (8 mRyd per interface unit cell) ✓

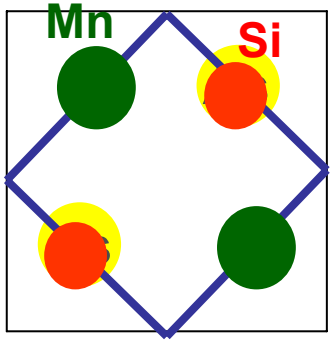
ideal MnSi/As interface

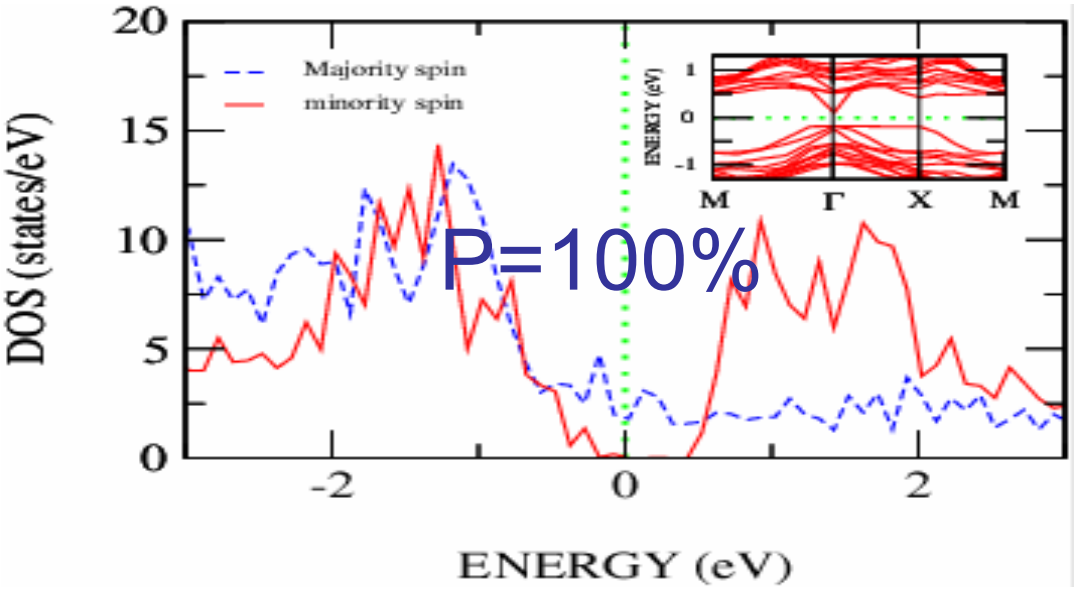
Mn(Ga)





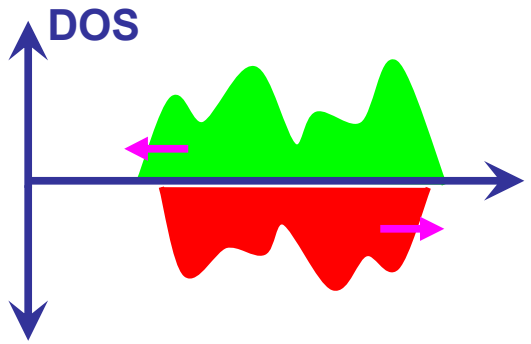
Mn(As)





Two main mechanisms for the variation of DOS in the interface region

- Exchange enhancement (lowering of the coordination number at the surface and interface increases the splitting of the Minority and majority DOS.)

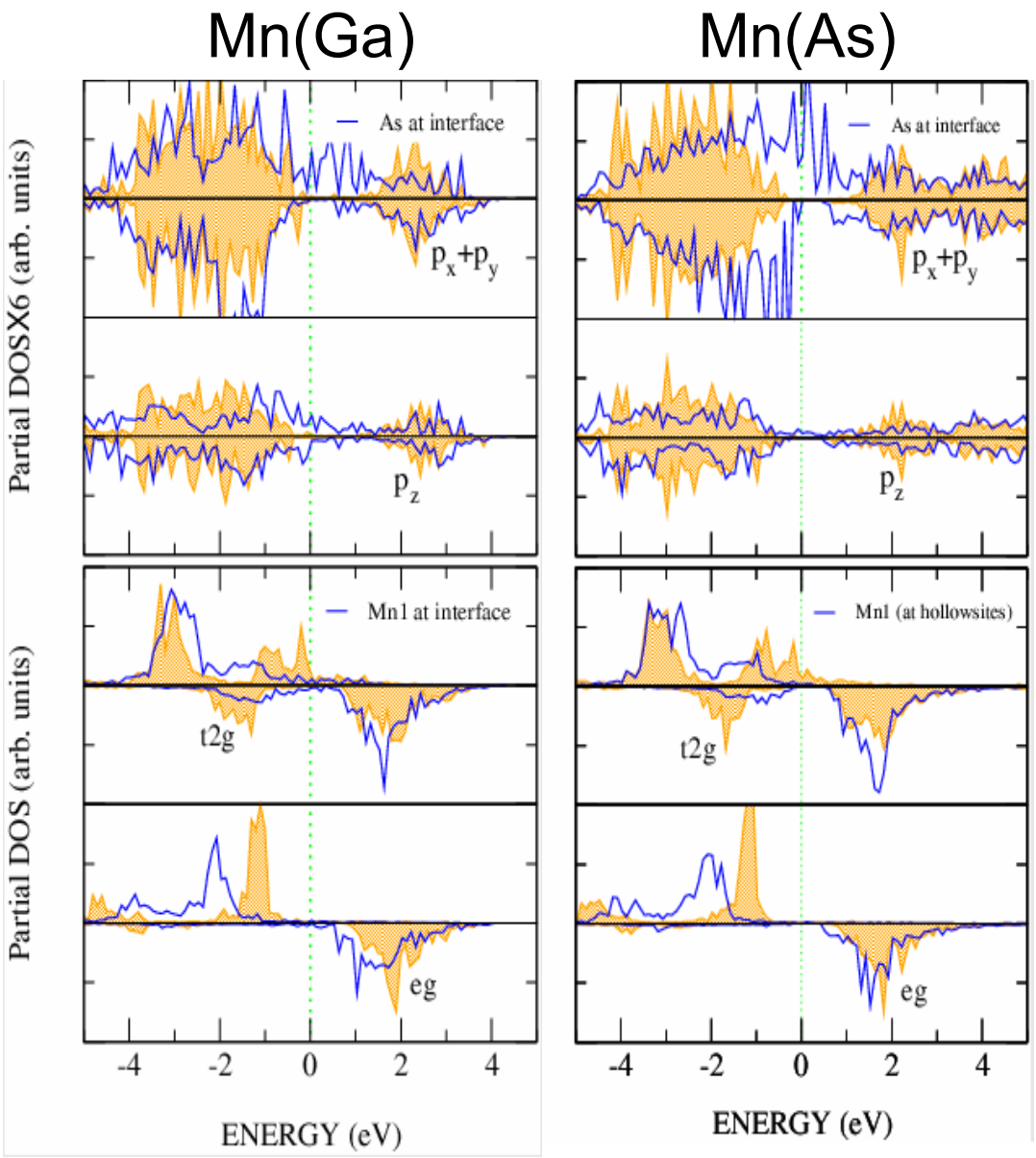


- Potential raise up (leads to the surface or interface potential barriers and shifts the corresponding DOS towards higher energies.)

Partial DOS

Potential raise up

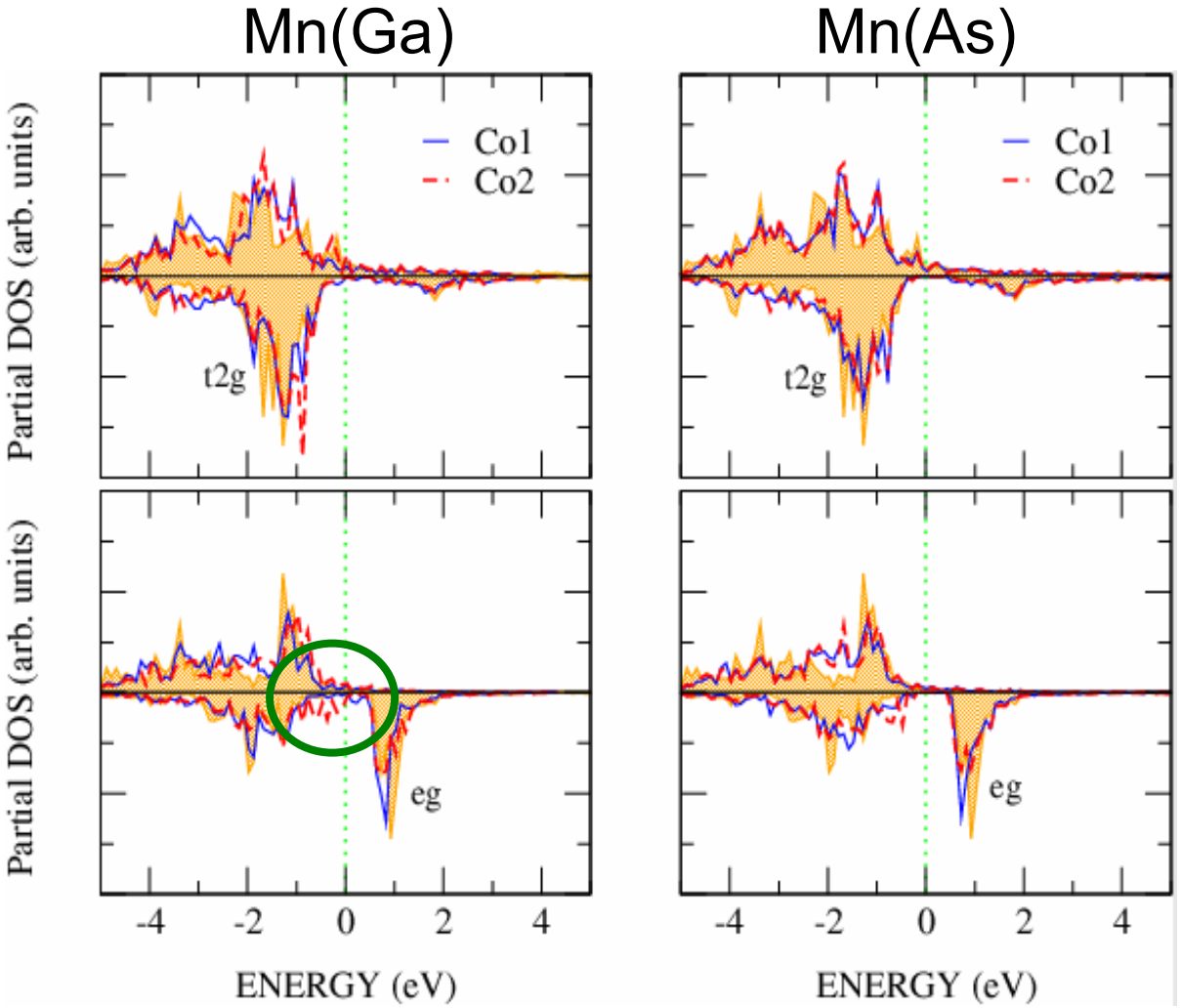
Exchange splitting



Partial DOS

2nd plane

Co1 continues the GaAs structure at 2nd plane

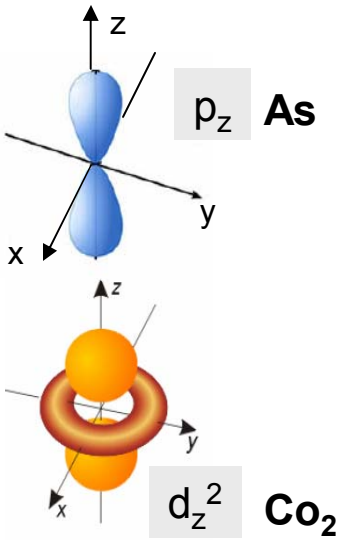


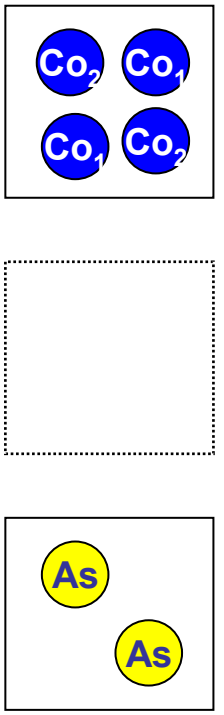
Why in eg of Mn(Ga) Co2 has more interface states than Co1?

What is the difference between Co1 and Co2 ?

Co_2 is at top site of As

Overlap between P_z of As and dz^2 of Co_2



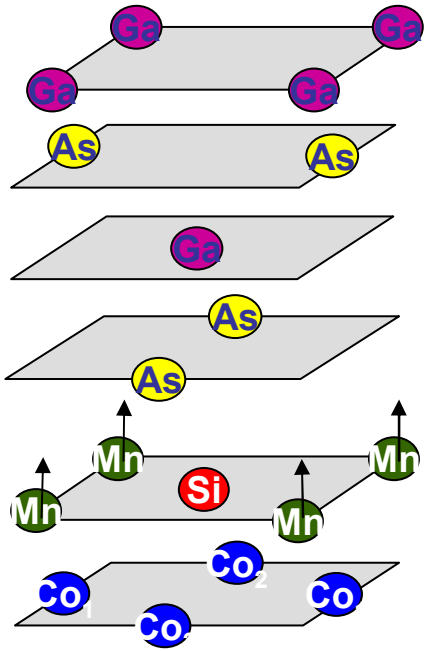


Why Mn(As) save half-metallicity while Mn(Ga) does not?

The origin of half-metallicity: d-d exchange interaction between Co and Mn [5].

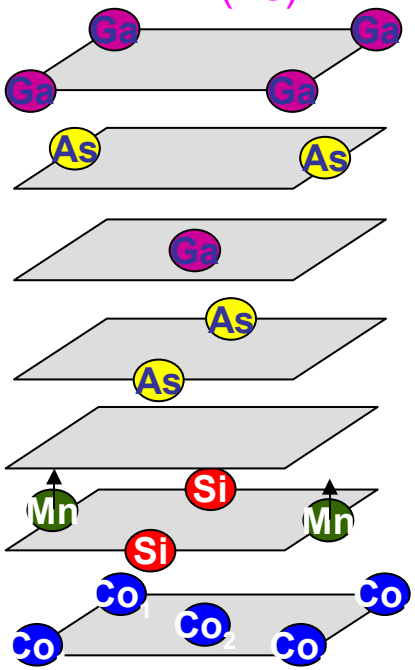
Interface

Mn(Ga)

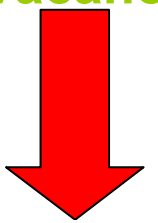


Interface

Mn(As)



Ga vacancy site



Mn-Co bond is weakend

& Mn-As bond enhanced

Mn-Co bond weakness is not large enough to destroy the half-metalicity!

P=100%

[5] Galanakis, et al. Phys. Rev B 66 , 174429 (2002)

Second conclusion

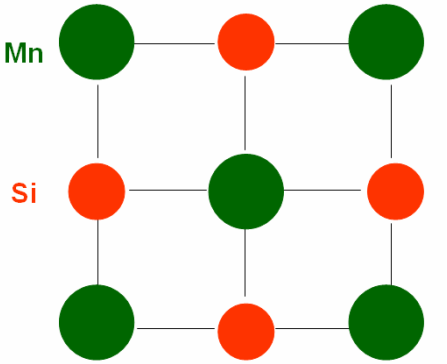
- 1. Mn(As) interface has a polarization of P=100% while the same termination in the $Co_2MnSi(001)$ surface has a lower polarization [4].

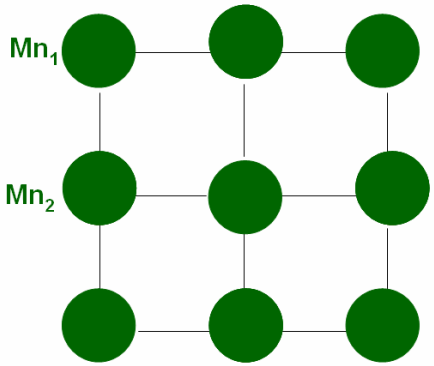
- 2. The interface states that decreases the Polarization of Mn(Ga) partly come from the Mn t2g states and mostly from Co eg states. The second one has the dominant role.

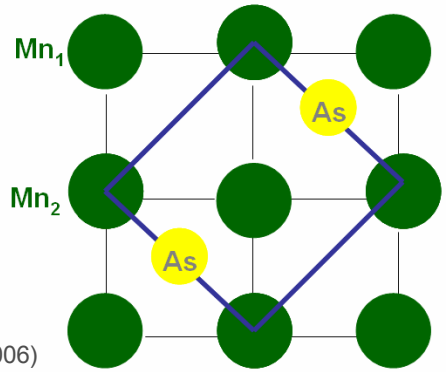
[4] S. J Hashemifar et al. PRl 94, 096402 (2005)

Mn segregation

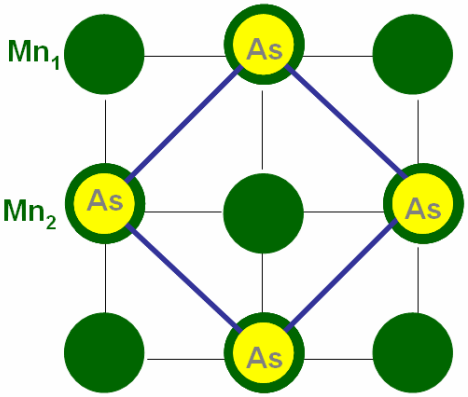
- Observation of the **Mn segragation to the interface [2].**
- **Presence of Mn_2As phase in the interface has been confirmed[3].**
- **Our computational study predicts that a cover of Mn layer on Co termination preserve the half metallicity [4].**







Mn(Ga)



Mn(As)

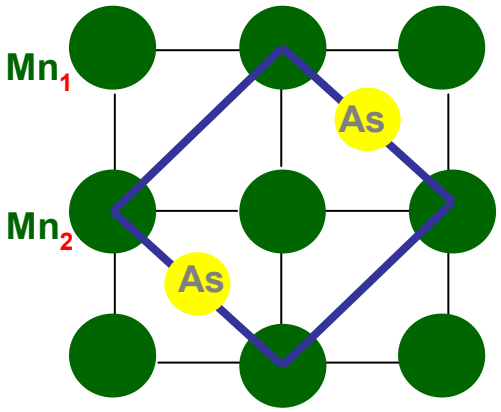
[2] wang et al, PRB 71, 144416 (2005)

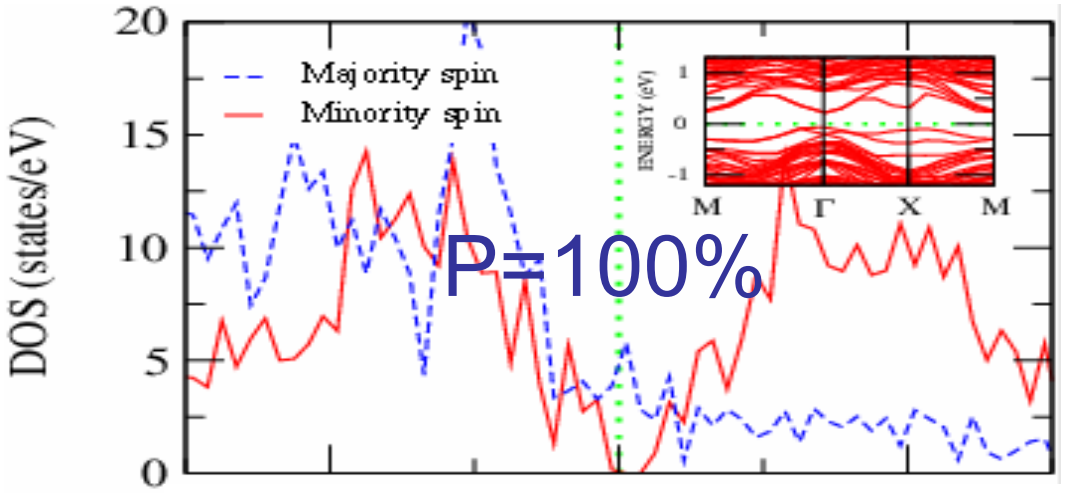
[3] L. J Singh et al, J, Appl. Phys 99, 013904 (2006)

[4] S. J Hashemifar et al. PRl 94, 096402 (2005)

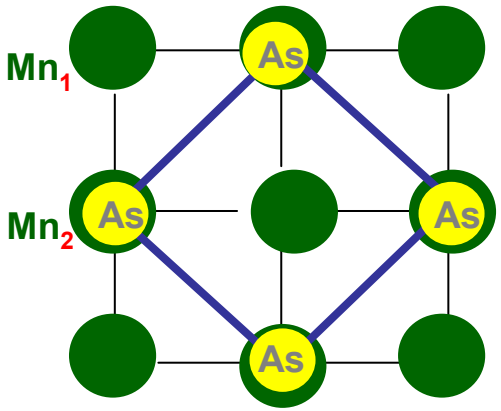
Modified MnMn/As interface

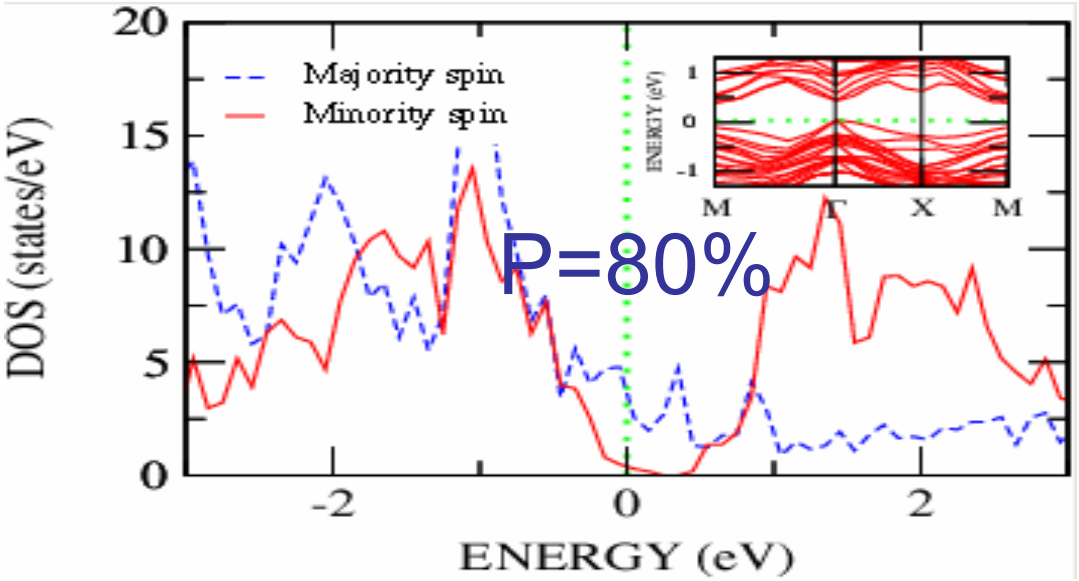
MnMn(Ga)





MnMn(As)

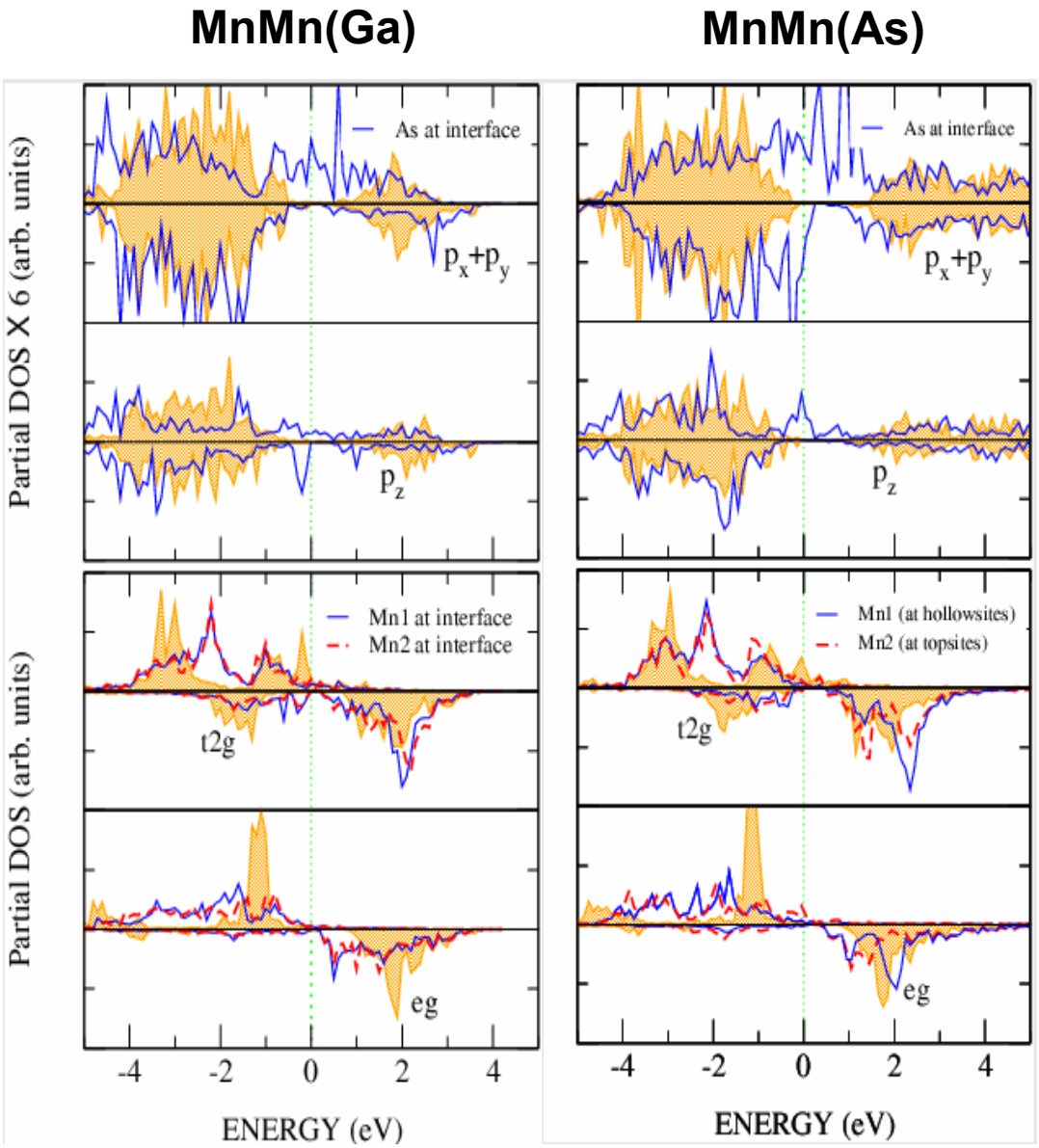




Partial DOS

Potential raise up

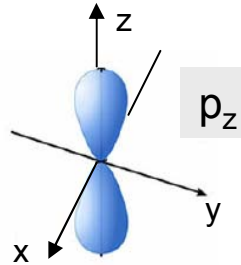
Exchange splitting



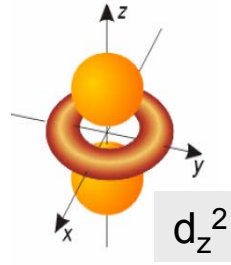
Partial DOS

2nd plane

Co1 continues the structure at 2nd plane

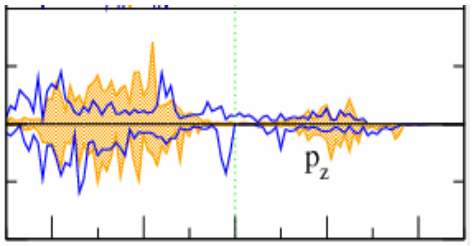


p_z **As**

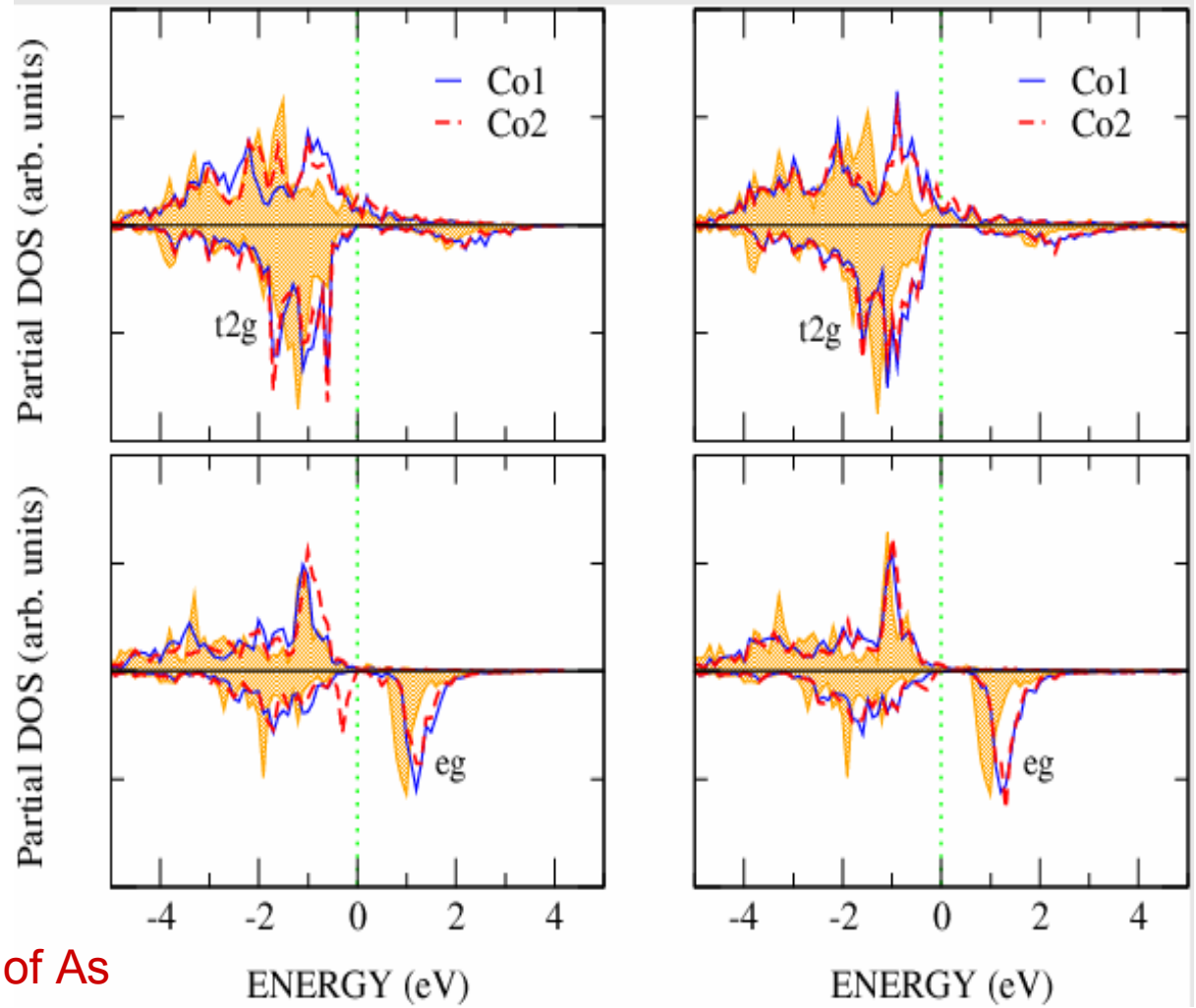


d_z^2 **Co_2**

As - p_z



MnMn(Ga) **MnMn(As)**



Co_2 is located at top site of As

- Ideal termination :

  P Mn(Ga)< P Mn(As)

  $E_{formation}$ Mn(Ga) ≤ $E_{formation}$ Mn(As)

- Modified termination :

  P Mn(Ga) > P Mn(As)

  $E_{formation}$ Mn(Ga) < $E_{formation}$ Mn(As)

Conclusion:

Modified Mn(Ga) **has a high P and a low energy**

an appropriate interface structure

Why MnMn(Ga) has P=100% while Mn(Ga) had a lower polarization?

d-d exchange interaction between Co and Mn is the origin of half-metallicity in Heusler alloys [5].

In the Mn(Ga) interface the interfacial Mn atoms lose half of their Co neighbors and the Mn-Co bond is weakend at the interface. Hence P is lower than 100%.

In modified MnMn(Ga) interface two Mn interact with one Co, this effect compensates the weakness of d-d exchange interaction of Mn and Co atoms at ideal Mn(Ga) interface and hence leads to P=100%.

[5] Galanakis, et al. Phys. Rev B 66 , 174429 (2002)

Why Mn(As) has P=100% while

MnMn(As) has a lower polarization ?

It was shown that at MnSi surface Mn-Co bond tends to be weak.

In Mn(As): This bond weakness is not large enough to destroy the half metallicity.

In MnMn(As): The new Mn (Mn_2) located at top site of As causes the potential raise up in the As DOS. The result of this effect is the production of additional states by As in the gap. This leads to decreasing of P.

Magnetic properties

In SiMn(As) interface:

1. Mn magnetic moment at interface is higher than its bulk value: lower coordination number
2. Co atoms have equal magnetic moments: similar environment; small roughening of Co-Co plane

In MnMn(As) interface:

1. Mn2 magnetic moment is near to its bulk value: Mn2 is at top site of As (close distance) and hence it has a strong interaction with As
2. Co atoms have different magnetic moments: different environment compared with ideal termination and also higher roughening of Co-Co surface.
3. As magnetic moment in MnMn(As) interface is higher than the corresponding value in SiMn(As). As is at top site of Mn2 (close distance) and hence it has a strong interaction with Mn2.

SiMn(As) interface

	$m(\mu_B)$ at interface	$m(\mu_B)$ in bulk
Mn	4.23	3.31
Si	-0.13	-0.12
Co_1	0.80	0.95
Co_2	0.83	0.95
As	-0.20	-

MnMn(As) interface

	$m(\mu_B)$ at interface	$m(\mu_B)$ in bulk
Mn_1	4.09	3.31
Mn_2	3.23	3.31
Co_1	1.01	0.95
Co_2	0.87	0.95
As	-0.39	-

Magnetic properties

In SiMn(Ga) interface:

1. Mn magnetic moment at interface is higher than its bulk value: lower coordination number
2. Co atoms have different magnetic moments: As is located at top site with respect to Co_2; different environment between Co_1 and Co_2

In MnMn(Ga) interface:

1. Mn1 and Mn2 magnetic moments are near to their bulk values: strong bond with As atom located at bridge site (in confirm with yang et al.)
2. Co atoms have different magnetic moments: different environment ; higher roughening of Co-Co layer with respect to ideal termination.

SiMn(Ga) interface

	$m(\mu_B)$ at interface	$m(\mu_B)$ in bulk
Mn	3.96	3.31
Si	-0.24	-0.12
Co_1	0.88	0.94
Co_2	0.73	0.94
As	-0.21	-

MnMn(Ga) interface

	$m(\mu_B)$ at interface	$m(\mu_B)$ in bulk
Mn_1	3.58	3.31
Mn_2	3.72	3.31
Co_1	1.04	0.94
Co_2	0.82	0.94
As	-0.23	-

FINAL CONCLUSION

1. MnSi/As termination is stable under appropriate conditions.

2. Co-Mn bond is stronger in Mn(As) compared to the Mn(Ga), hence half-metallicity is preserved in Mn(As) structure.

3. A pure Mn intermediate layer protects well half-metallicity in MnMn(Ga) while in MnMn(As) the half-metallicity is destroyed due to the effect of potential raise up on As.

Acknowledgement

The fruitful collaboration with Profs. Peter. Kratzer[1] and Mathias Scheffler[1] during the first part of this work (surface study) is acknowledged.

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

- Ghaderi, Hashemifar, Akbarzadeh, Peressi, submitted to Phys. Rev. B
- Hashemifar, Kratzer, Scheffler, Phys. Rev. Lett. **94** (2005) 096402

- Akbarzadeh , Hashemifar, ICTP-IUT school on Electronic-structure calculations and their applications in materials science, Isfahan, April 26 - May 6, 2005
- Kratzer, Hashemifar, Wu, Scheffler, American Physical Society March meeting, March 2005, Los Angeles, USA
- Hashemifar , Akbarzadeh , The 7th condensed matter conference of the physical society of Iran, January 2005, Tehran
- Hashemifar, Kratzer, Scheffler, The 20th General Conference of the Condensed Matter Division European Phys. Soc., July 2004, Prague, Czech Republic

THANKS

Electrostatic Potential

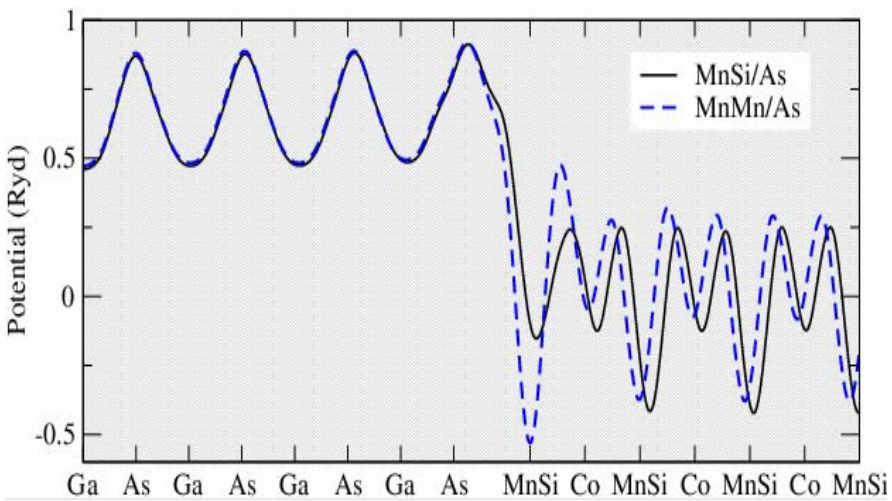
Periodic geometry in the planes perpendicular to the growth direction.

⇕

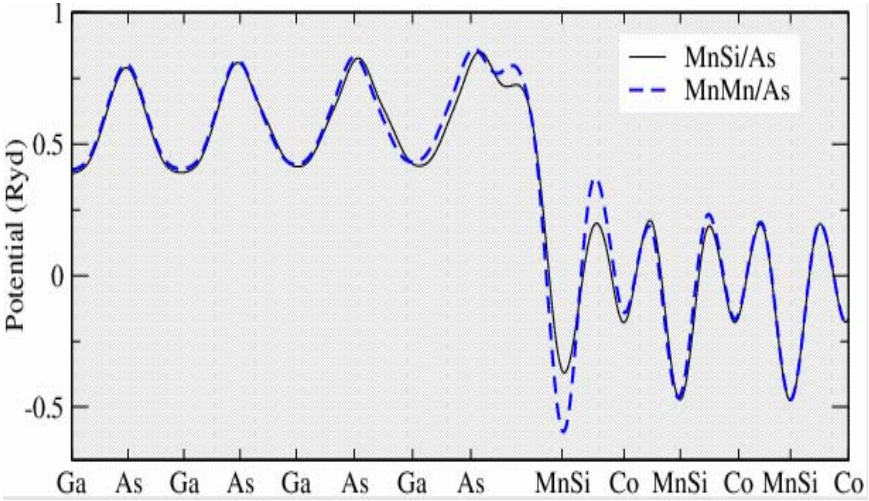
xy planar average : $V^{(planar)}(z) = \frac{1}{S}\int_S V(x,y,z)dxdy$

- **Two periodic functions join smoothly across the interface.**
- **Interfacial effects are related to the difference between these periodic functions.**

Mn(Ga)



Mn(As)



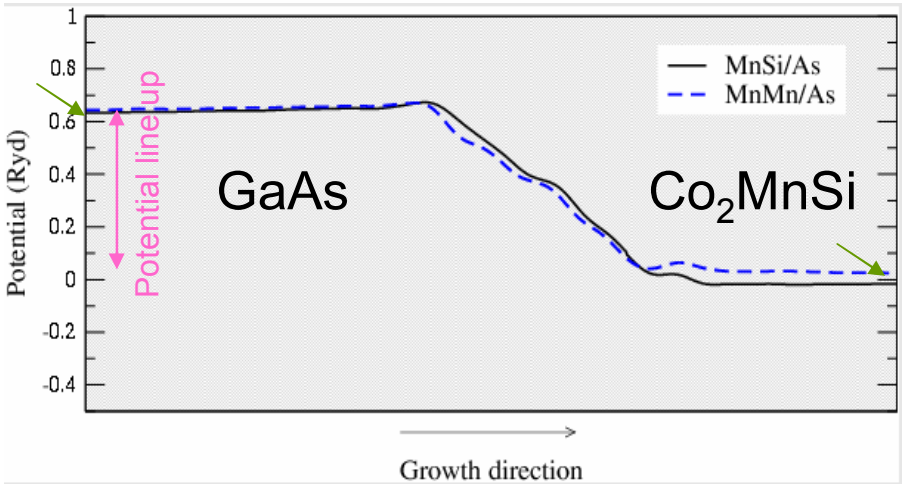
Electrostatic Potential

Macroscopic average : **(to get rid of the bulk-like oscillations)**

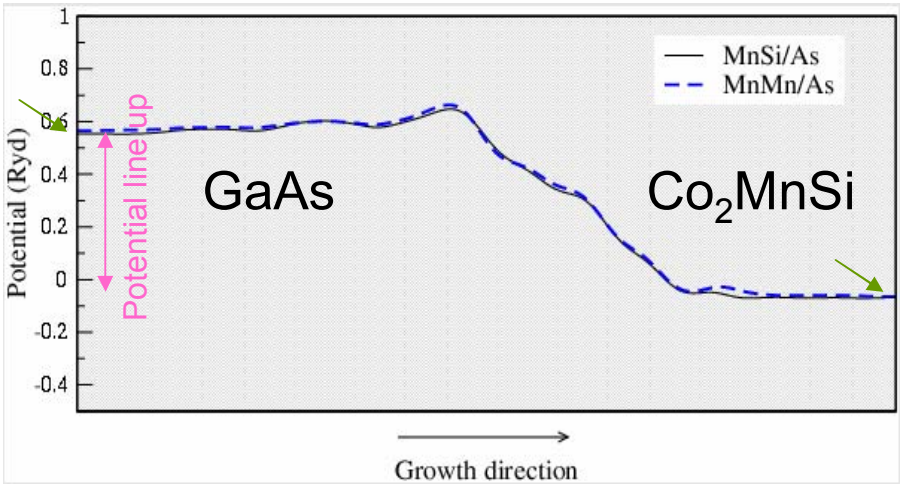
$$V^{(macro)}(z) = \frac{1}{a}\int_{z-a/2}^{z+a/2} V^{(planar)}(z')dz'$$

$$a = \text{lattice parameter}$$

Mn(Ga)



Mn(As)



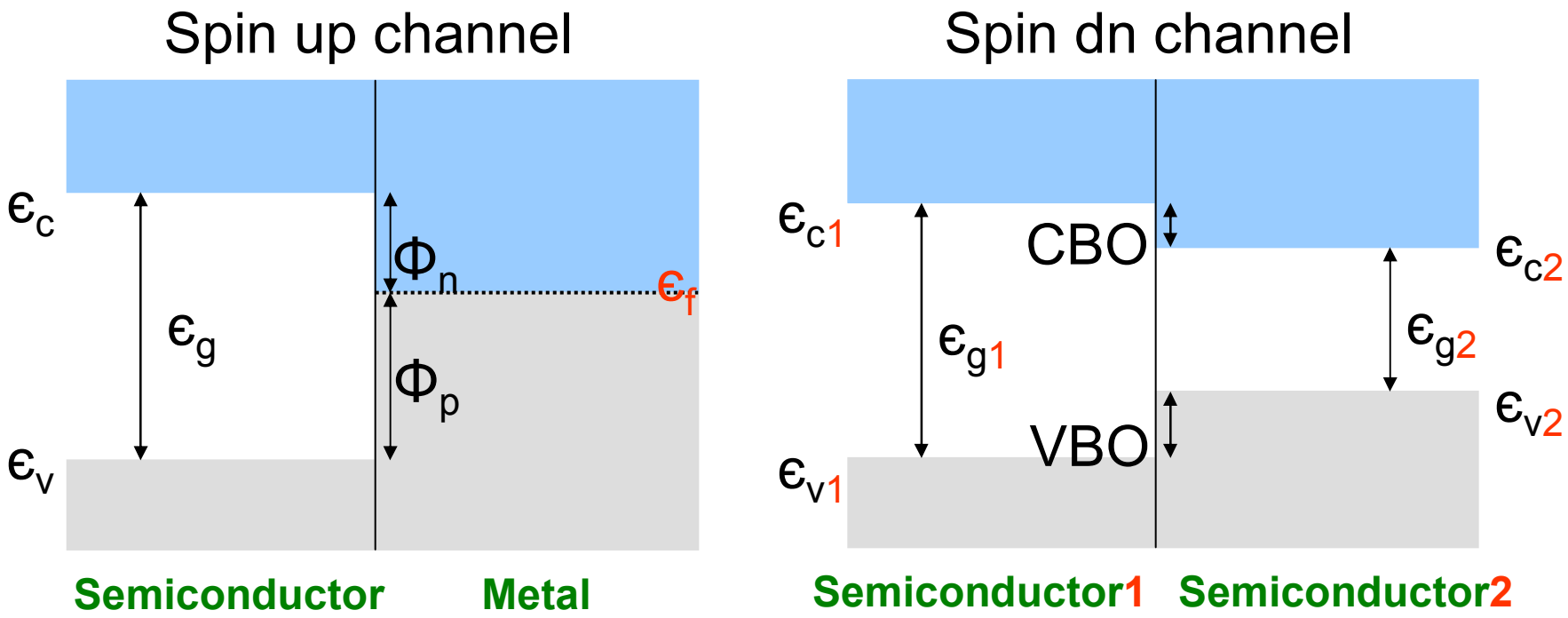
Band alignment at interfaces

(general explanation)

Control the transport properties

whether or not one can tune the transport properties

by Manipulating the band line-ups ???



Band alignments at Co2MnSi/GaAs(001) interface

SiMn-As termination ; Mn(As) pattern

bulk :

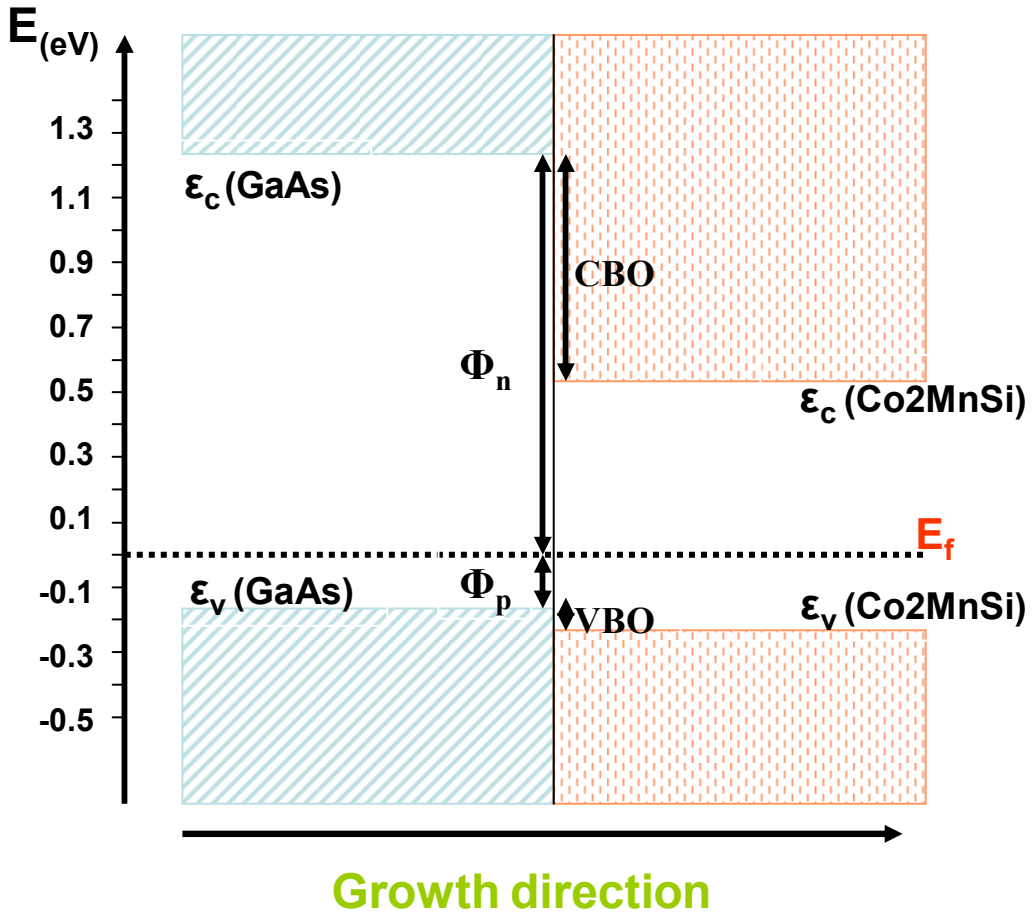
$$\Delta E_p = E_V^{GaAs} - E_f^{Co_2MnSi}$$

$$\Delta E_V = E_V^{GaAs} - E_V^{Co_2MnSi}$$

Interface :

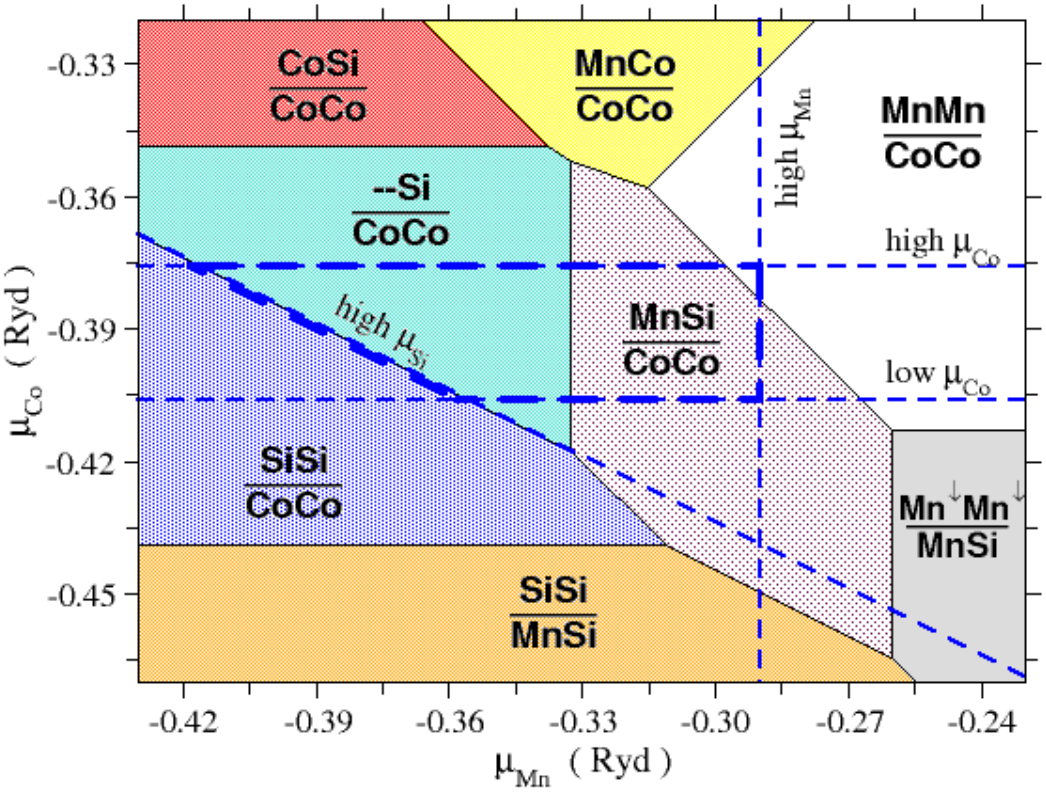
$$\Phi_p = \Delta E_p + \Delta V$$

$$VBO = \Delta E_V + \Delta V$$



The experimental band gap of GaAs (1.42eV) is added to get the CBO in the minority spin channel and Φ_n

Phase Diagram



- MnSi, MnMn, SiSi, --Si surfaces could be stabilized
- Mn deficiency is the most probable disorder of ideal MnSi surface
- Presence of Cobalt on surface leads to high instability

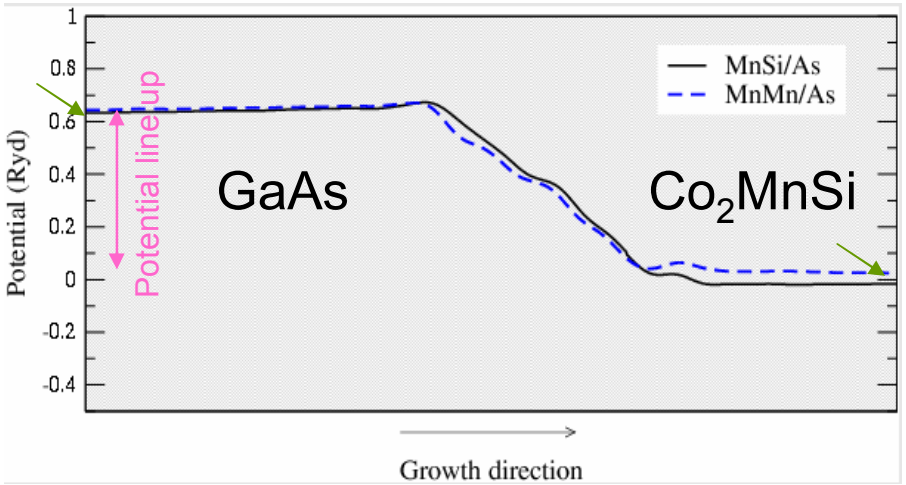
Electrostatic Potential

Macroscopic average : **(to subtract the bulk-like oscillations)**

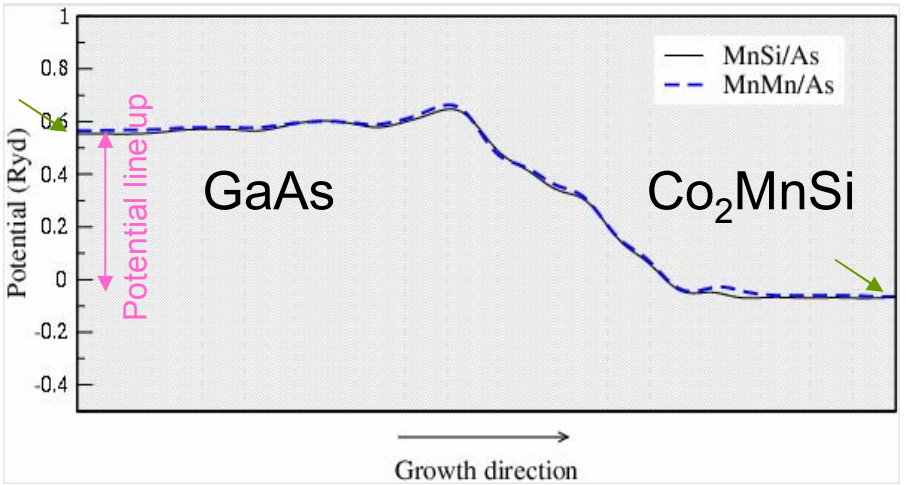
For any microscopic quantity $f^{(micro)}(z)$ we can define a macroscopic average $f^{(macro)}(z)$:

$$V^{(macro)}(z) = \int_{-\frac{a}{2}}^{\frac{a}{2}} V^{(micro)}(z')dz'$$

Mn(Ga)



Mn(As)



Electrostatic Potential

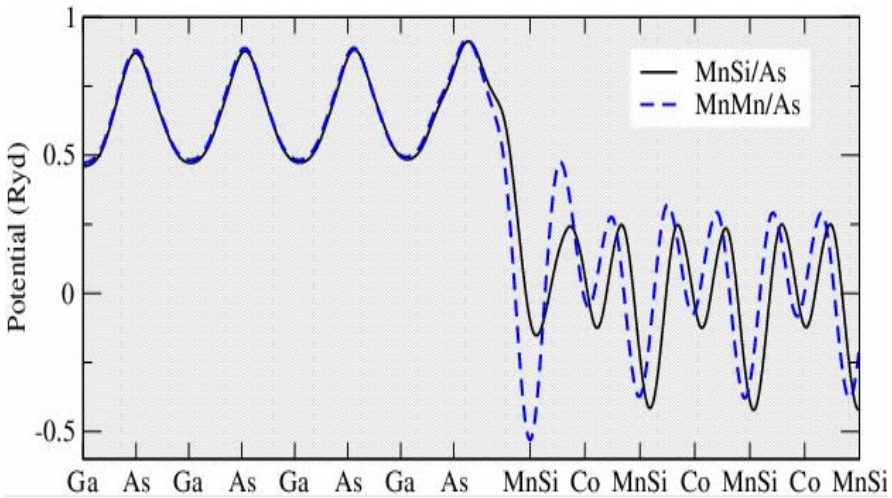
Periodic geometry perpendicular to the growth direction.

⇕

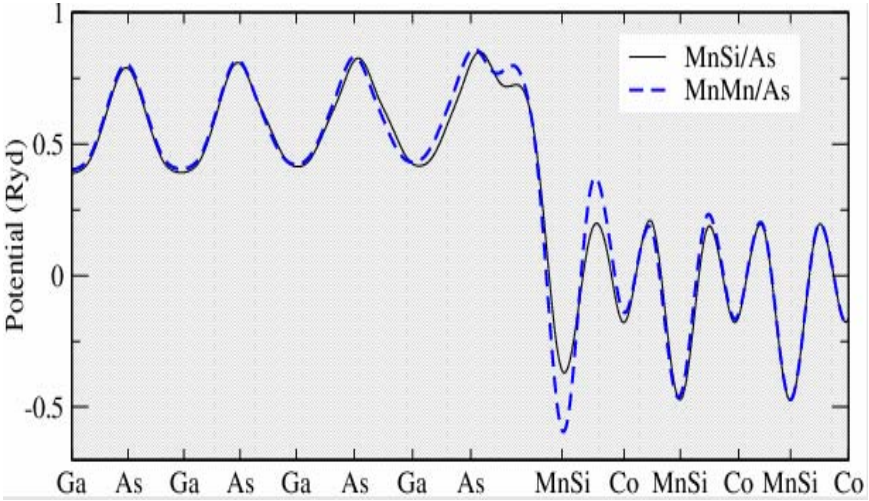
xy planar average : $\overline{V}(z) = \frac{1}{S}\int_S V(x,y,z)dxdy$

- **Two distinct periodic functions join across the interface and interfacial effects are related to the difference between these periodic functions.**

Mn(Ga)



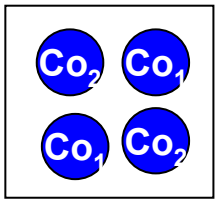
Mn(As)



Why in eg of Mn(Ga) Co2 has more surface states than Co1?

What is the difference between Co1 and Co2 ?

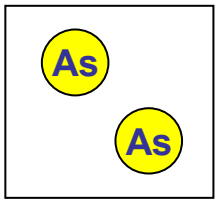
Co_2 at top site with respect to As



More surface state at Co2 eg

especially at dz^2

(due to the overlaping with p_z of As)

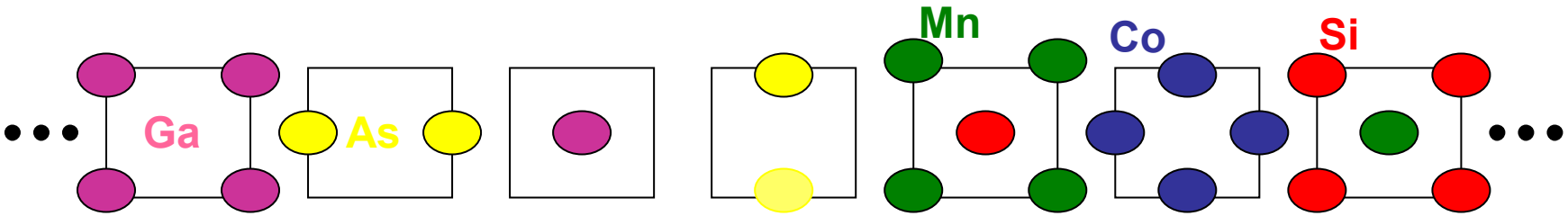


	2nd plane(CoCo)
Mn(Ga)	0.08
Mn(As)	0.02

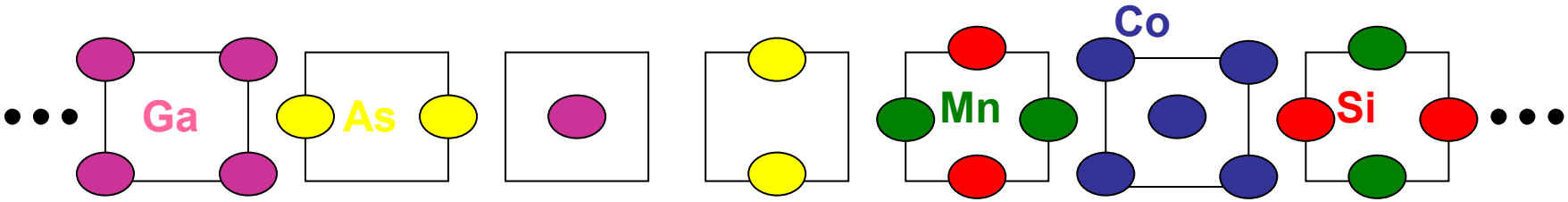
roughening $\rightarrow A^{\circ}$

Higher roughening ~ more environmental difference for Co1 and Co2

MnSi/As termination



Mn on Ga sublattice



Mn on As sublattice