Chapter 3
Lecture 12: Diluted Magnetic Semiconductors

Outline

- **Introduction to Spintronics**
- Introduction to DMS
- Subsurfactant Epitaxy of DMS Materials
- Non-Compensated n-p Codoping of DMS Materials

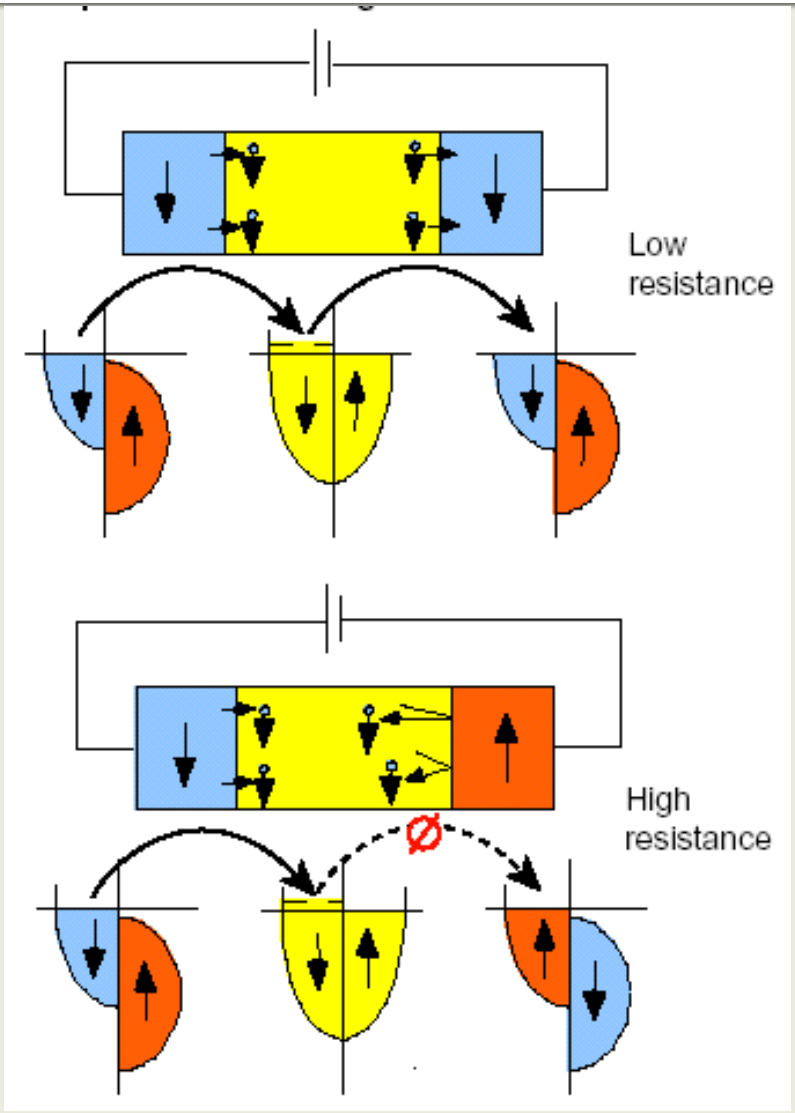
SPINTRONICS WORLD

METALS 1987-		SEMICONDUCTORS 1998-
? ? ?	PARA	SPIN-FET Q-BITS
AMR GMR TMR	FERRO (Collective)	AMR GMR TMR +++

Spin-polarized device principles (metallic layers):

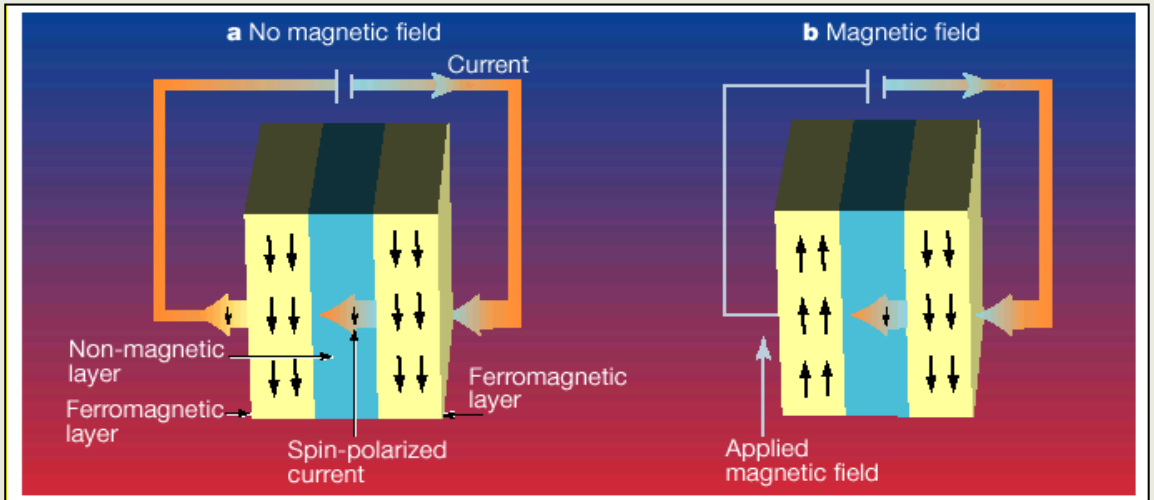
Parallel magnetic layers
$\Rightarrow \downarrow$ spins can flow

Antiparallel magnetic layers
$\Rightarrow \downarrow$ spins cannot flow



[Prinz, Science **282**, 1660 (1998)]

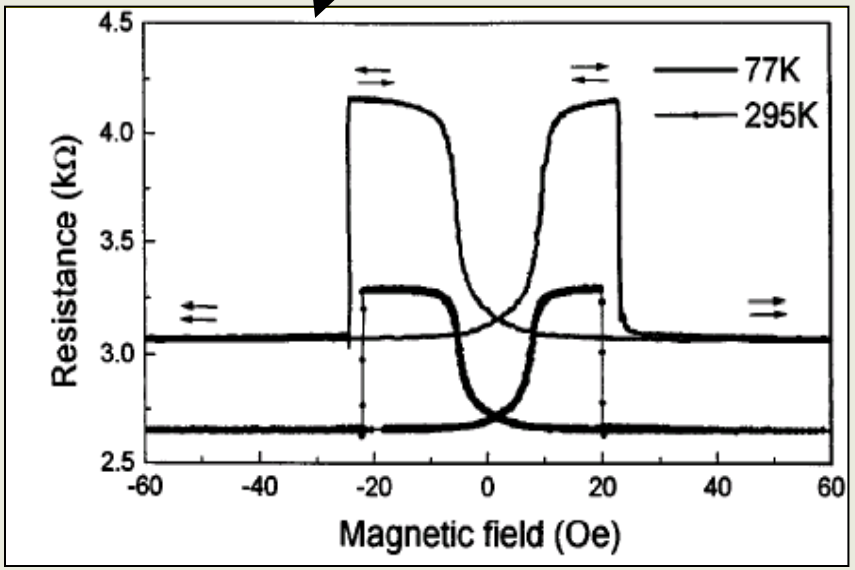
FERROMAGNETIC METALS



A spin valve in action. a, With no magnetic field, the spin-polarized current can flow. b, When a magnetic field is applied, the spin-polarized current cannot pass through both ferromagnetic layers.

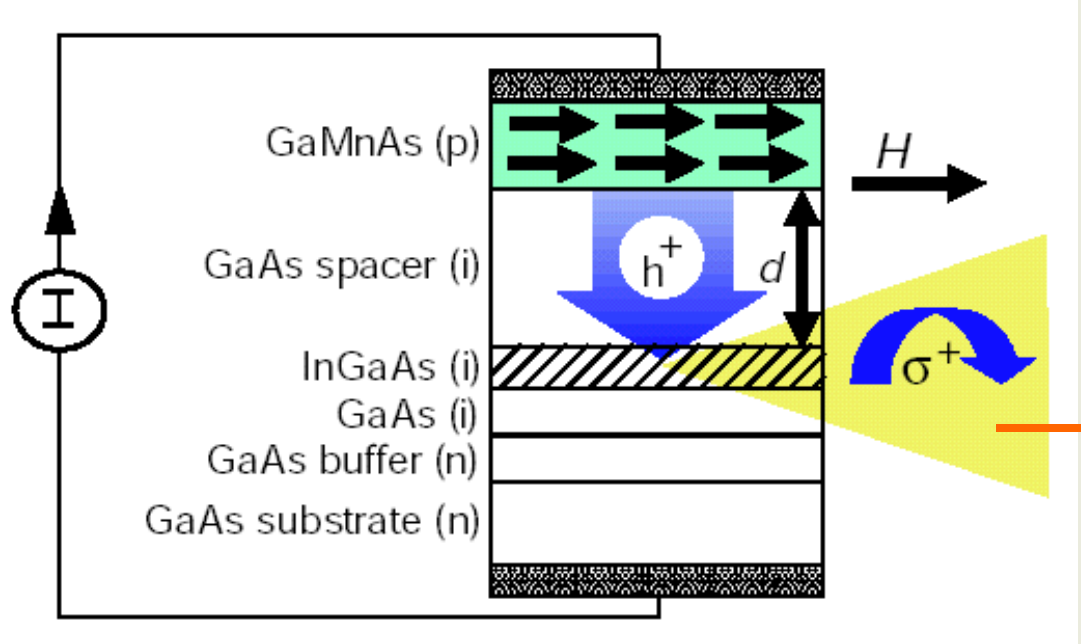
Spin valve GMR

Ferro-Insulator-Ferro TMR



Spin injection into a FM semiconductor heterostructure

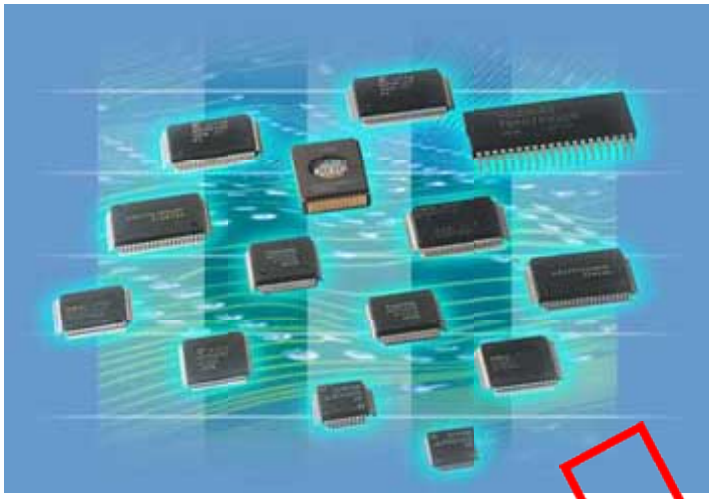
Spin transfer



Polarization of emitted electrolumiscence determines spin polarization of injected holes

Ohno et al., Nature 402, 790 (1999)
Malajovich et al., Nature 2001

Dream Technology Integration

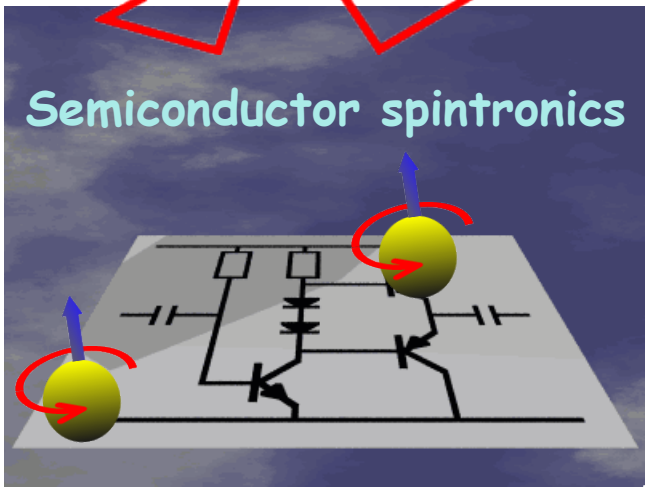


Silicon era

Magnetism and GMR

Injection of spin-polarized carriers plays important role in device applications:

- Combination of semiconductor technology with magnetism gives rise to new devices;
- Long spin-coherence times (~ 100 ns) have been observed in semiconductors



- smaller
- faster
- low power
- non-volatile
- multi-functionality

Outline

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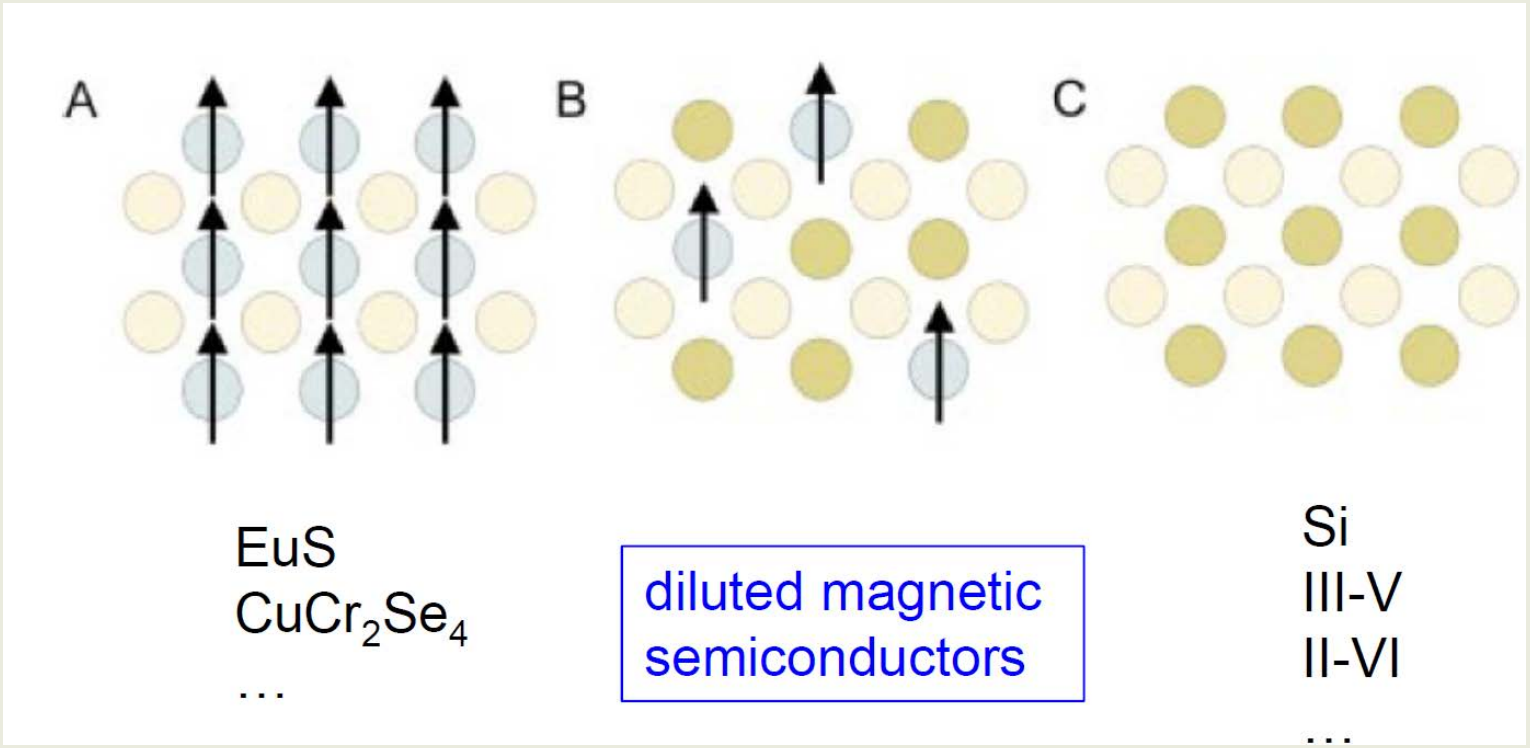
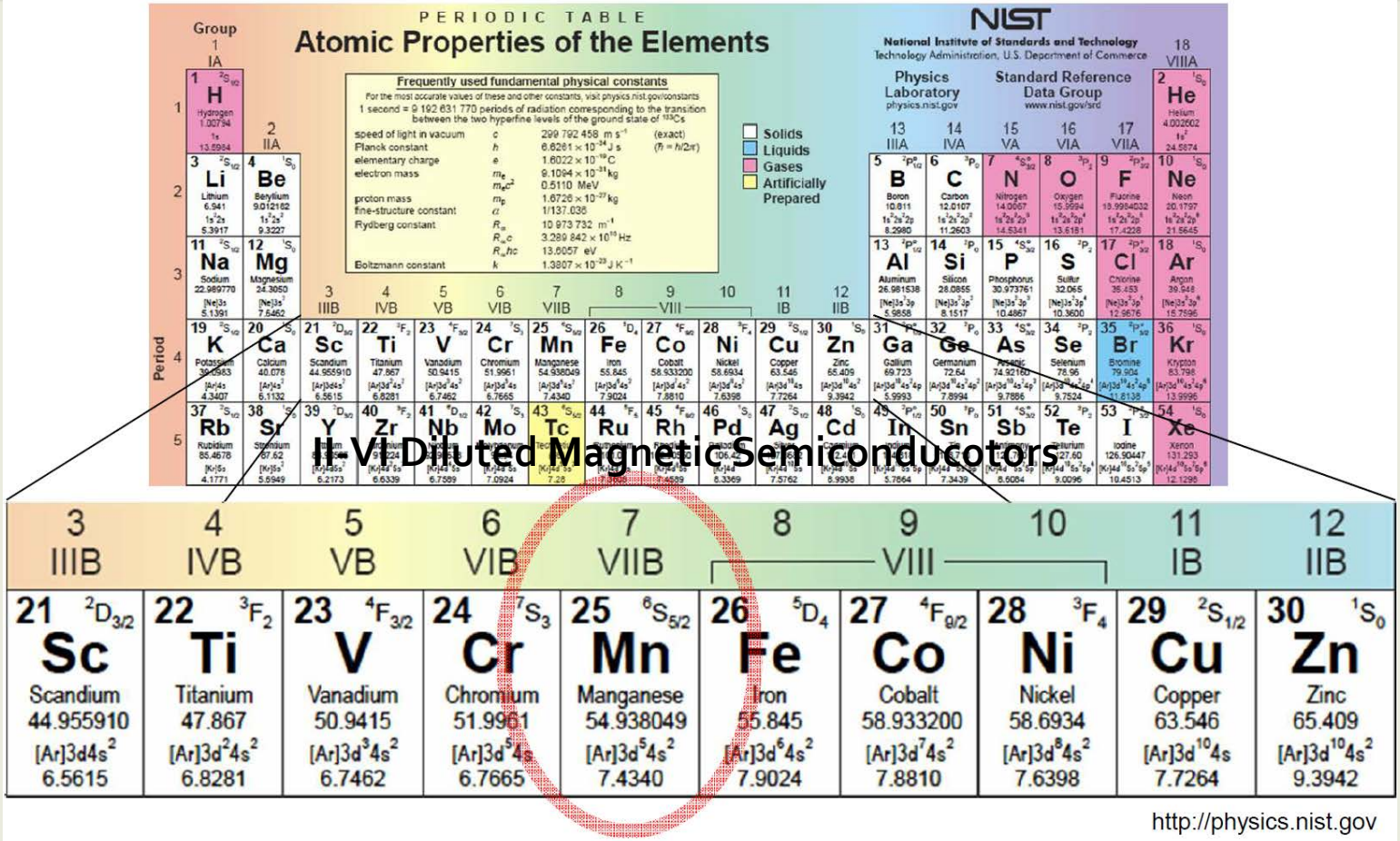
- **Introduction to DMS**
- Subsurfactant Epitaxy of DMS Materials
- Non-Compensated n-p Codoping of DMS Materials

Making semiconductor magnetic: Doping



Magnetic ion: Mn



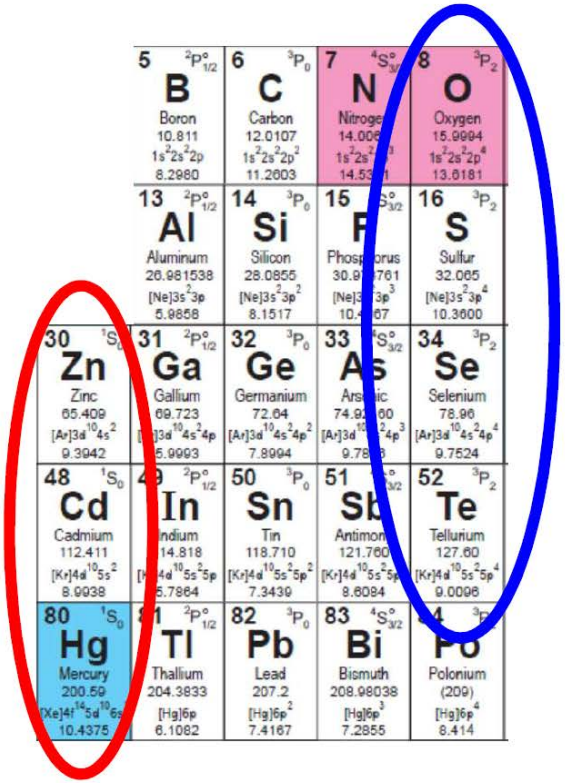
Hund rule: Distributing n electrons over $2(2l+1)$ degenerate atomic orbitals, the lowest energy state is the state that maximize the total spin angular momentum S

Mn: l=2, n=5 -> S=5/2

Magnetic Semiconductors

- **Early 60's: EuO and $CdCr_2S_4$**
  $\Rightarrow$ very hard to grow
- **Mid-80's: Diluted Magnetic Semiconductors**
  II-VI (e.g., CdTe and ZnS) II $\rightarrow$ Mn
  $\Rightarrow$ difficult to dope
  $\Rightarrow$ direct Mn-Mn AFM exchange interaction
  PM, AFM, or SG (spin glass) behavior
  $\Rightarrow$ present-day techniques: doping has led to FM for $T < 2K$
  IV-VI (e.g., PbSnTe) IV $\rightarrow$ Mn
  $\Rightarrow$ hard to prepare (bulk and heterostructures), but helped understand the mechanism of carrier-mediated FM
- **Late 80's: MBE $\rightarrow$ uniform (In,Mn)As films on GaAs substrates:**
  FM on p-type.
- **Late 90's: MBE $\rightarrow$ uniform (Ga,Mn)As films on GaAs substrates:**
  FM; heterostructures
- **2000~** ZnO:X, GaN:X, TiO2: X (X=TM, RE), CdMnGeP2, ZnCrTe
  Searching ferromagnetism with high Tc.

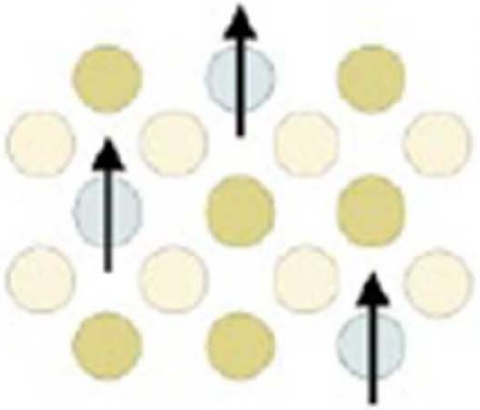
II-VI Diluted Magnetic Semiconducotors

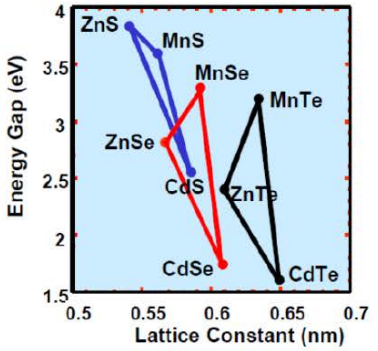


+

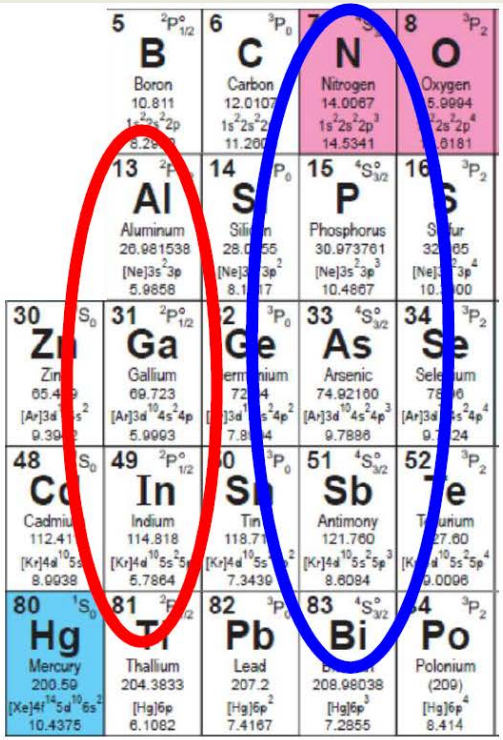
25 $^6S_{5/2}$
Mn
Manganese
54.938049
$[Ar]3d^5 4s^2$
7.4340

=





III-V Diluted Magnetic Semiconducotors



+

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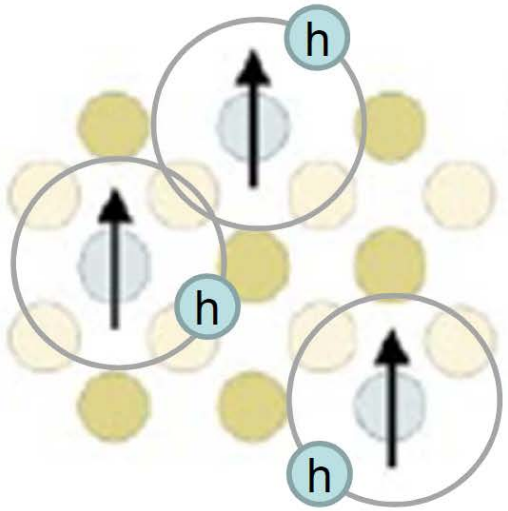
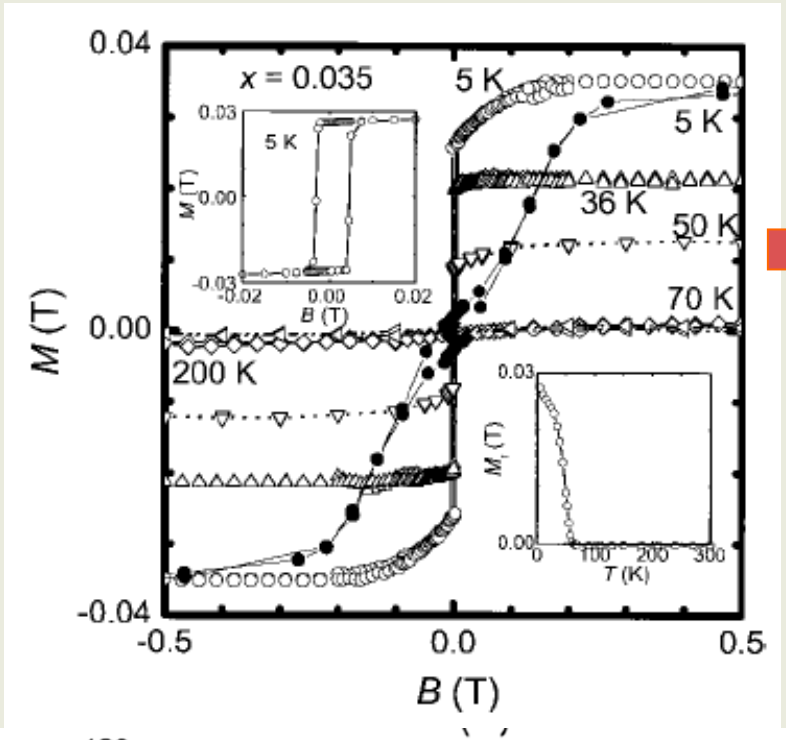


not to scale

(Ga,Mn)As, (In,Mn)As, (Ga,Mn)Sb

Mn-doped GaAs

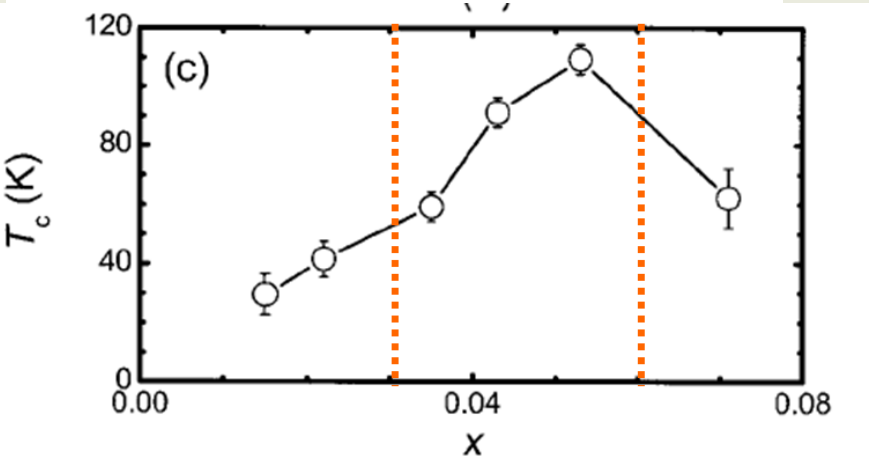


x = 0.035

Open symbols: B in-plane

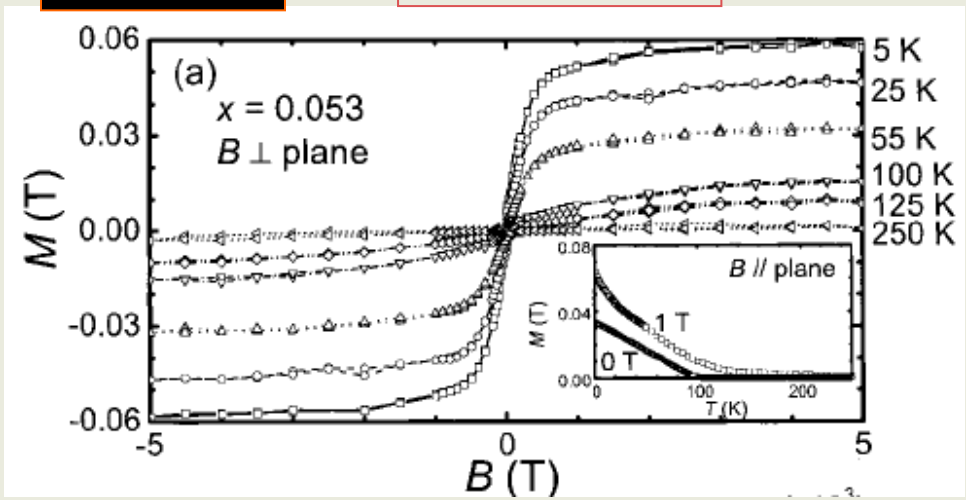
- hysteresis ⇒ FM with easy axis in plane;
- remanence vs. $T \Rightarrow T_c \sim 60$ K

[Ohno, JMMM **200**, 110(1999)]



x = 0.053

$T_c \sim 110$ K



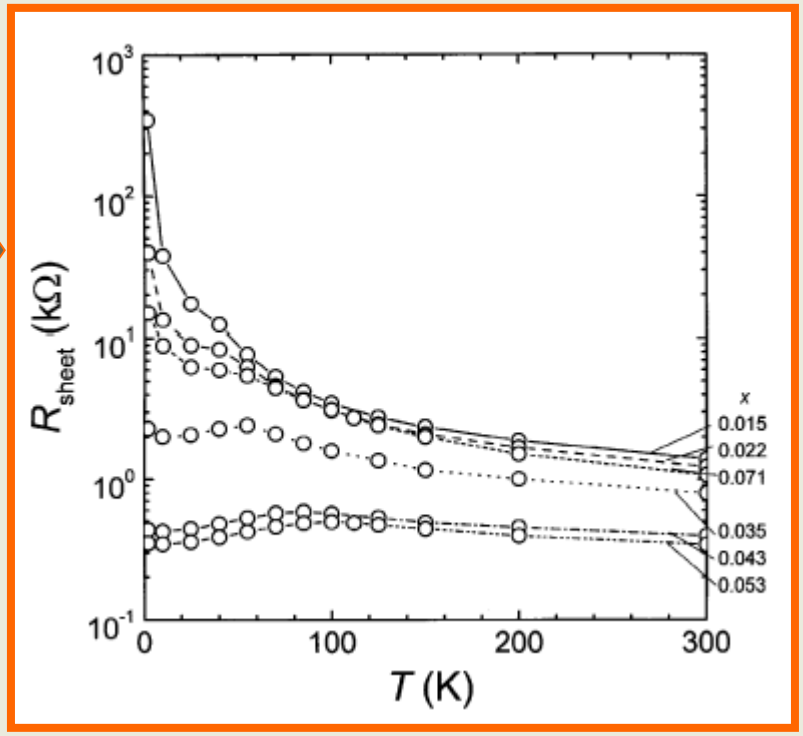
Mn-doped GaAs

Resistance measurements on samples with different Mn concentrations:

Metal $\rightarrow R \downarrow$ as $T \uparrow$

Insulator $\rightarrow R \uparrow$ as $T \uparrow$

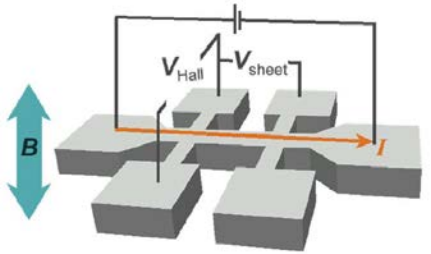
$\Rightarrow$ Reentrant MIT



[Ohno, JMMM **200**, 110(1999)]

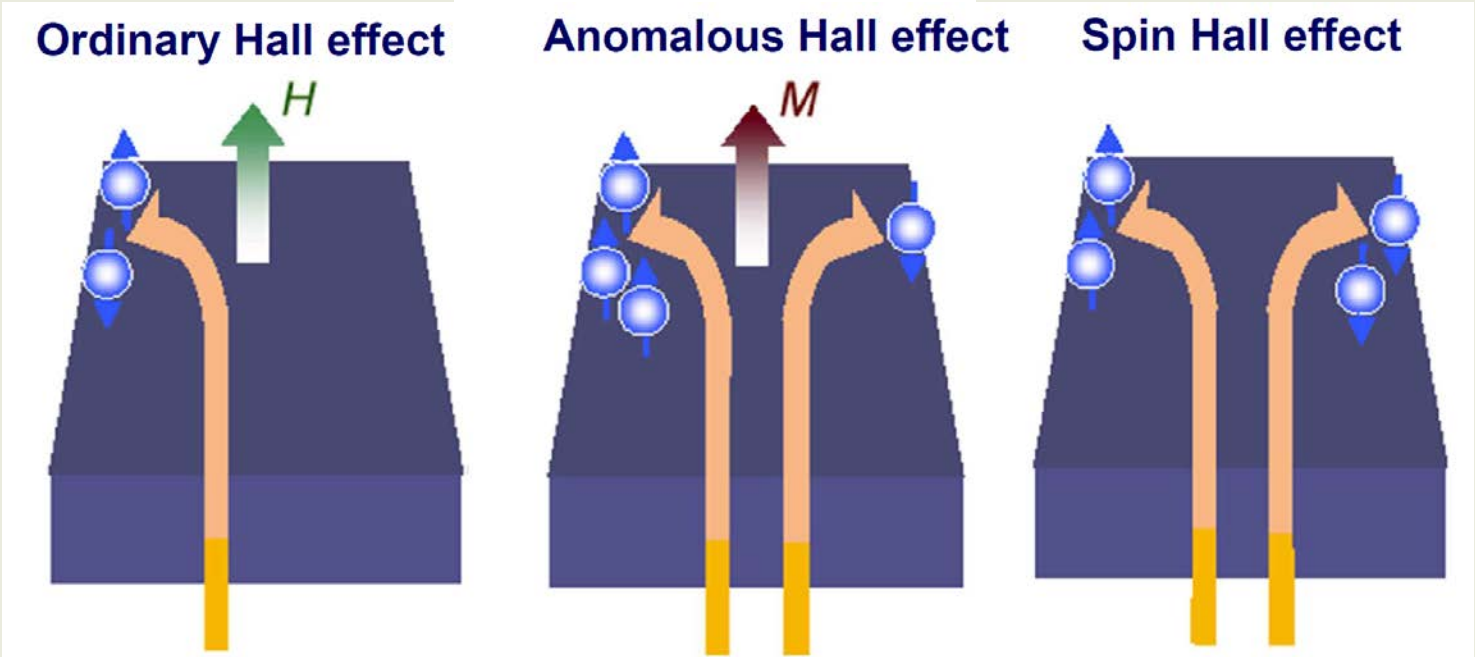
Transport of (Ga,Mn)As

$$R_{\mathrm{Hall}} = (R_0/d)B + (R_S/d)M_\perp$$



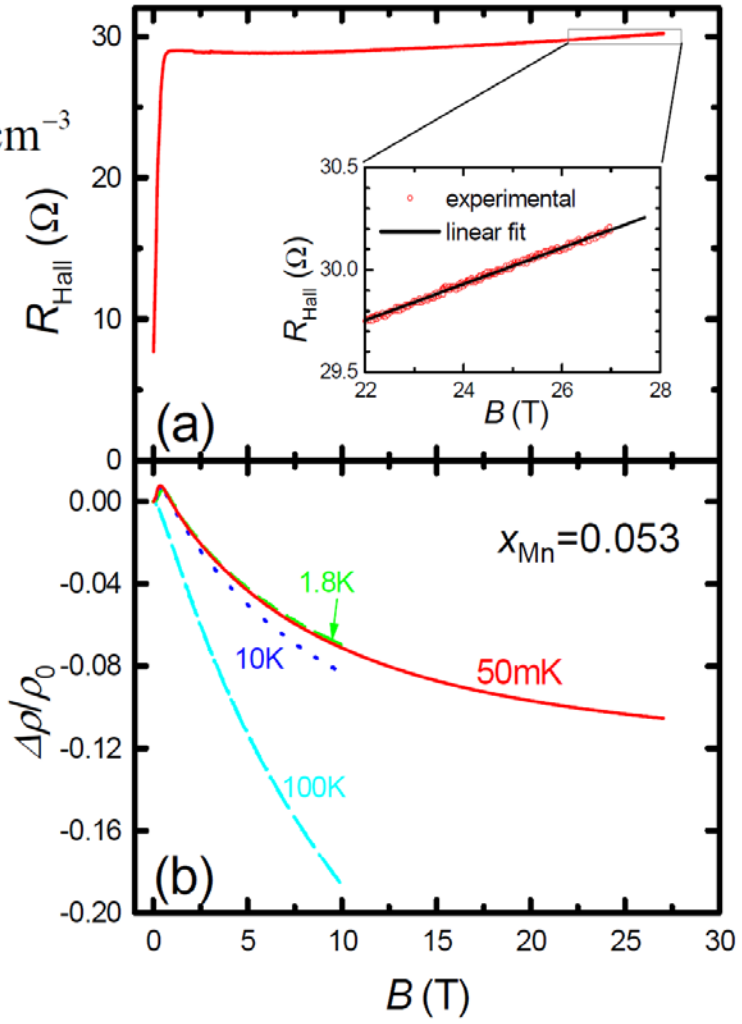
$$R_{\mathrm{Hall}} = V_{\mathrm{Hall}}/I$$
$$R_{\mathrm{sheet}} \propto V_{\mathrm{sheet}}/I$$

Hall Effects



$Ga_{0.947}Mn_{0.053}As$

$[Mn] = 1.2 \times 10^{21}\ \mathrm{cm}^{-3}$



p = 3.5 x 10^{20} cm^{-3}
(30% of Mn)

$$\Delta\rho_{Hall} = \Delta(R_0 B + R_S M_\perp)$$
$$\approx R_0 \Delta B$$
$$= \frac{1}{qpd}\Delta B$$

T. Omiya et al. *Physica E*, 2000

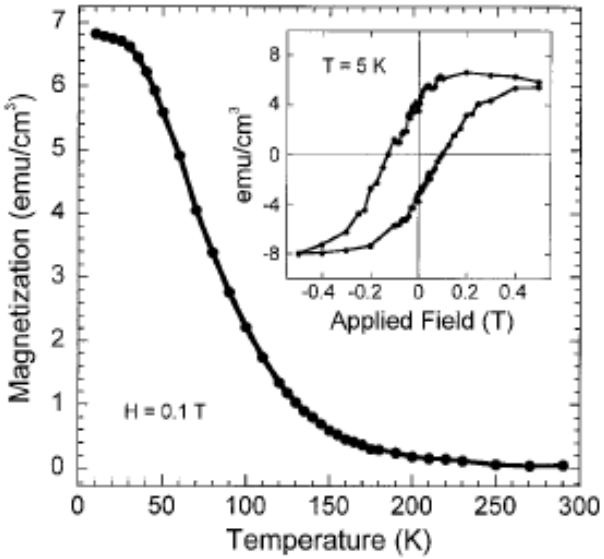
Silicon-Compatible DMS

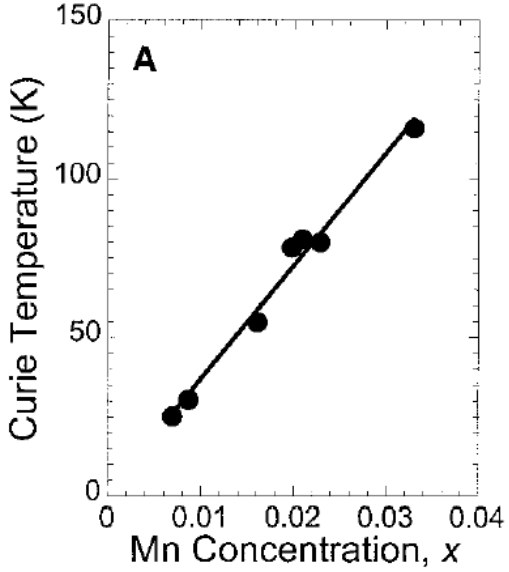
A Group-IV Ferromagnetic Semiconductor: Mn_xGe_{1-x}

Y. D. Park,* A. T. Hanbicki, S. C. Erwin, C. S. Hellberg, J. M. Sullivan, J. E. Mattson,† T. F. Ambrose,‡ A. Wilson,§ G. Spanos, B. T. Jonker‖

Naval Research Laboratory, Washington, DC

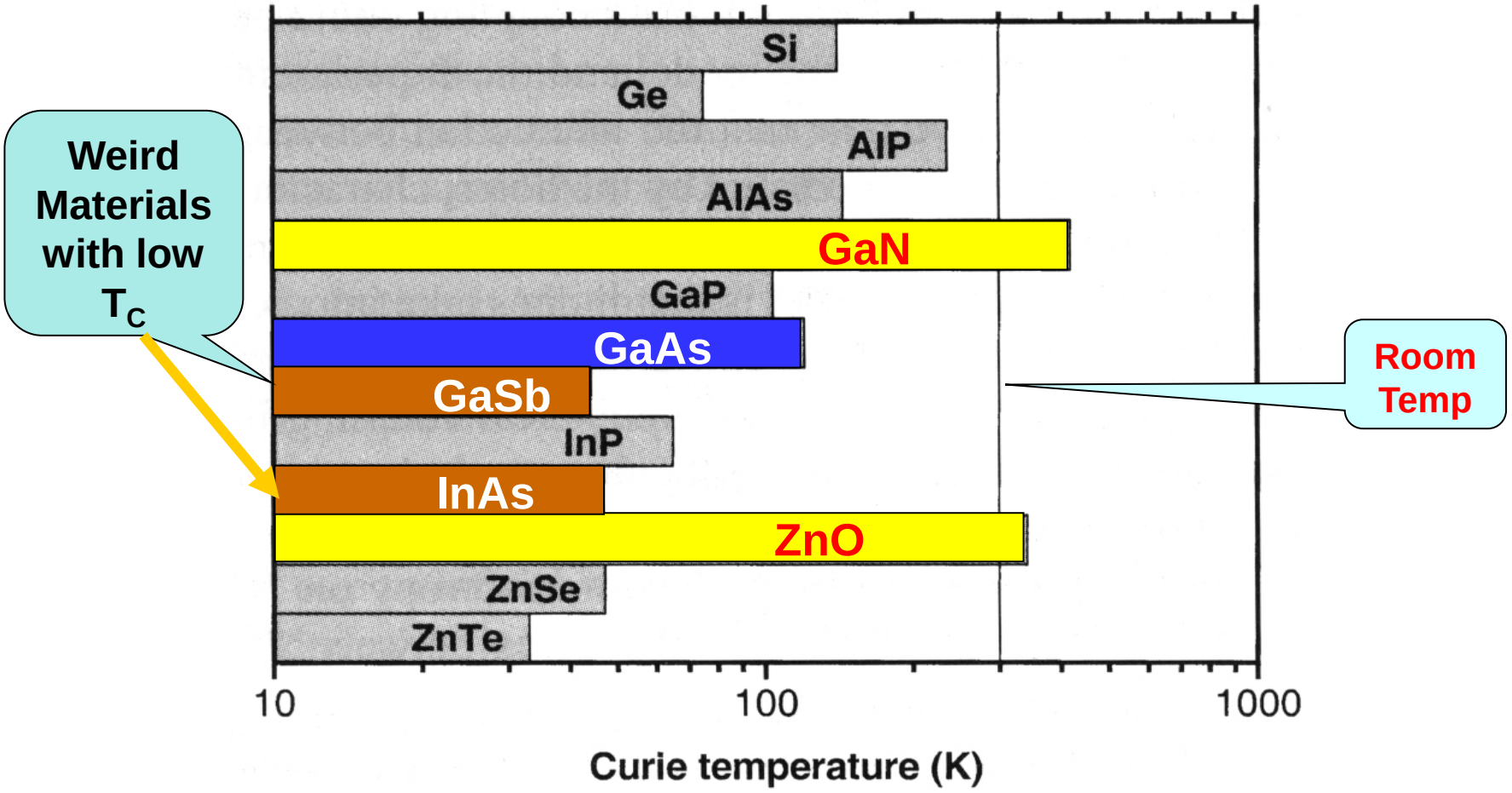
SCIENCE VOL 295 25 JANUARY 2002





$T_C \sim 116K << RT$

Predicted Curie Temperatures



Dietl *et al.*, Science , (2000)

Primary Challenge: Increase T_C to Room Temperature or Higher

Generic guides:

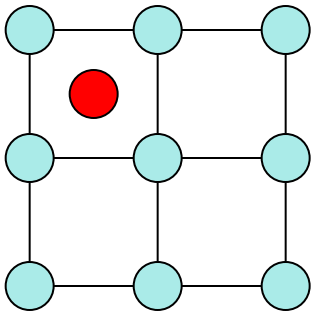
- "...any strategy that increases the hole density near Mn ions will increase Tc…"

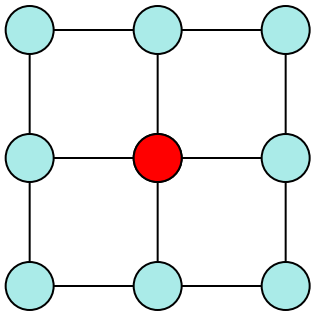
See: MacDonald, et al. Rev. Modern Phys. (2006)

- "…more substitutional, less interstitials…"

Interstitial

BAD





Substitutional

GOOD

See: C.Timm, J. Phys. Condens. Matter 15, R1865(2003)

Two New Recipes to Increase Substitutional Mn Doping in Ge

A. Subsurfactant Epitaxy

Prediction:

Wenguang Zhu, H. H. Weitering, E. G. Wang, E. Kaxiras, Z. Zhang, Phys. Rev. Lett. 93, 126102 (2004).

A detailed presentation of the theory see: Hua Chen, Wenguang Zhu, E. Kaxiras, Z. Zhang, PRB (2009)

Confirmation with a pleasant surprise:

Changgan Zeng, Z. Zhang, K von Benthem, M. F. Chisholm, H. H. Weitering, Phys. Rev. Lett. (2008)

B. Aided by Conventional Electronic Dopants (non-compensated n-p codoping)

Wenguang Zhu, Z. Zhang, E. Kaxiras, PRL (2008) & more

Sequential Multiscale Theoretical Approaches

- **Calculations of activation barriers within DFT:**
  - Vienna *ab initio* simulation package (VASP)
    Hafner, et al., ‘94-96.
  - “Climbing Image Nudged Elastic Band” (NEB)
    Jonsson et al., ‘98-00.

- **Kinetic Monte Carlo simulations of growth:**
  - Physically realistic growth conditions
    Voter, ‘86
    Metiu, Lu, & Zhang, ‘92.

- **Continuum: classical nucleation theory & elasticity**

Philosophy:

Structural control at nonmagnetic level, hoping for optimal magnetic properties as emergent phenomena

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- **Subsurfactant Epitaxy of DMS Materials**
- Non-Compensated n-p Codoping of DMS Materials

Subsurfactant Epitaxy: Collaborators

Theory

Dr. Wenguang Zhu
ICQS/ORNL
Harvard
UT

Hua Chen
UT

Prof. Tim Kaxiras
Harvard

Prof. Enge Wang
ICQS, CAS

Experiment

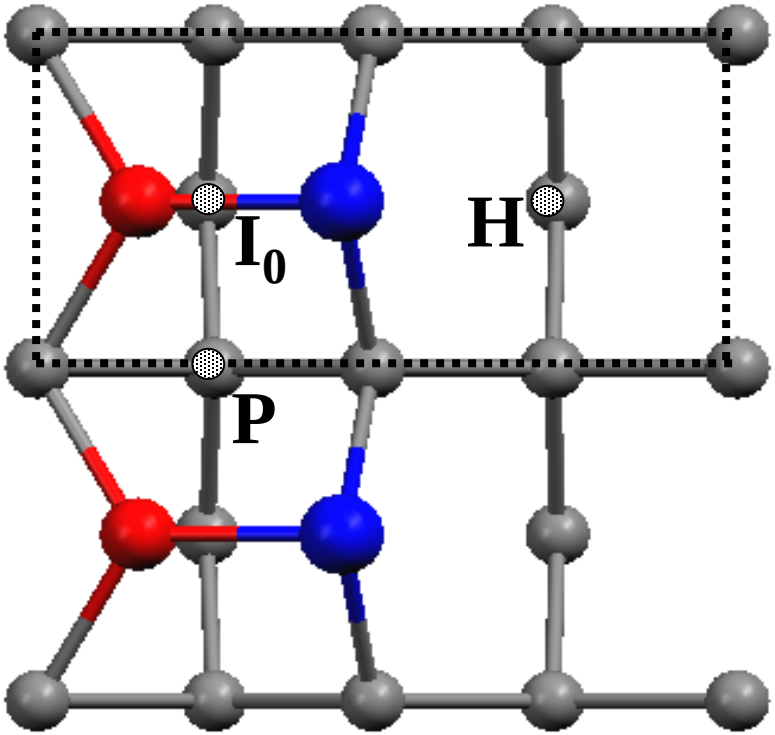
Dr. Changgan Zeng
UT

Prof. Hanno Weitering
UT/ORNL

Dr. Klaus van Benthem
Dr. Matthew Chrisholm
ORNL

Mn/Ge(100)-2x1: Growth Front Energetics and Kinetics

Top View

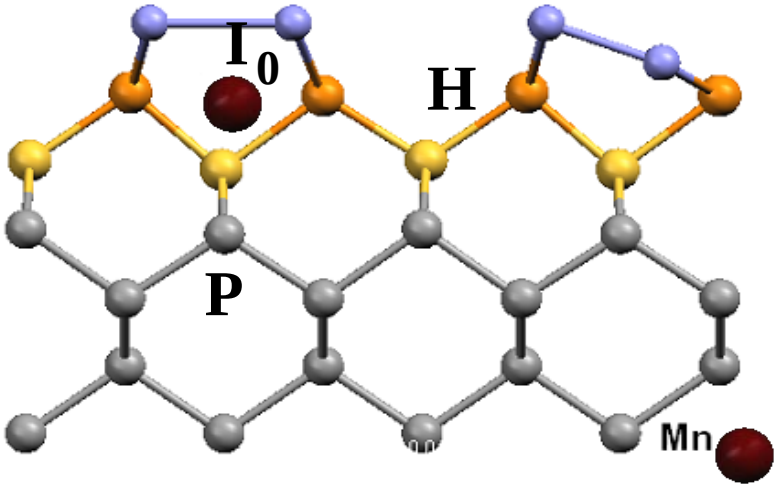


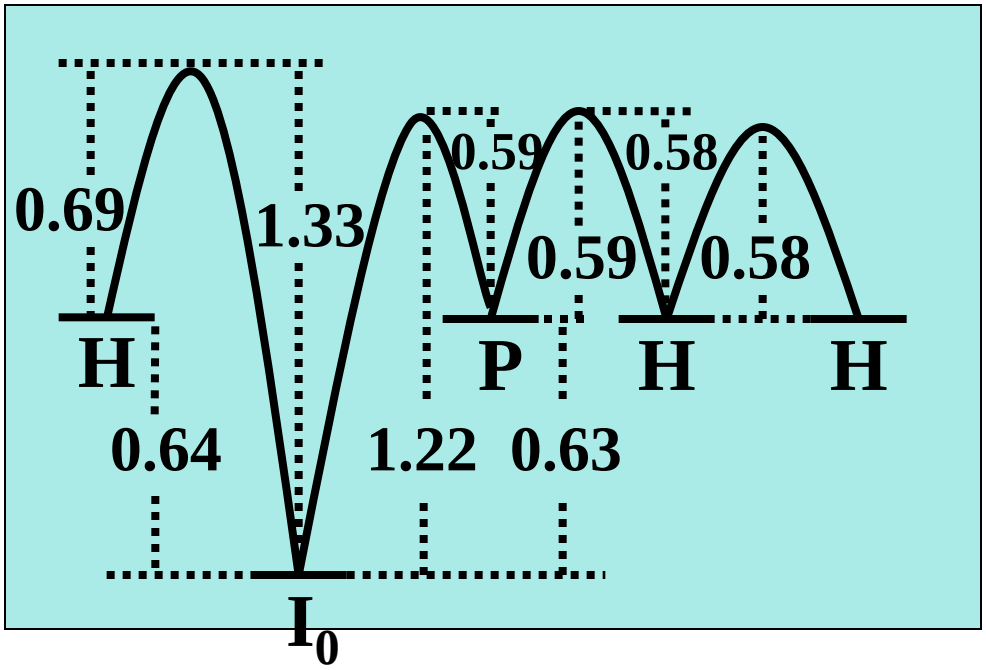
Ge up-atom deeper layer

Ge down-atom

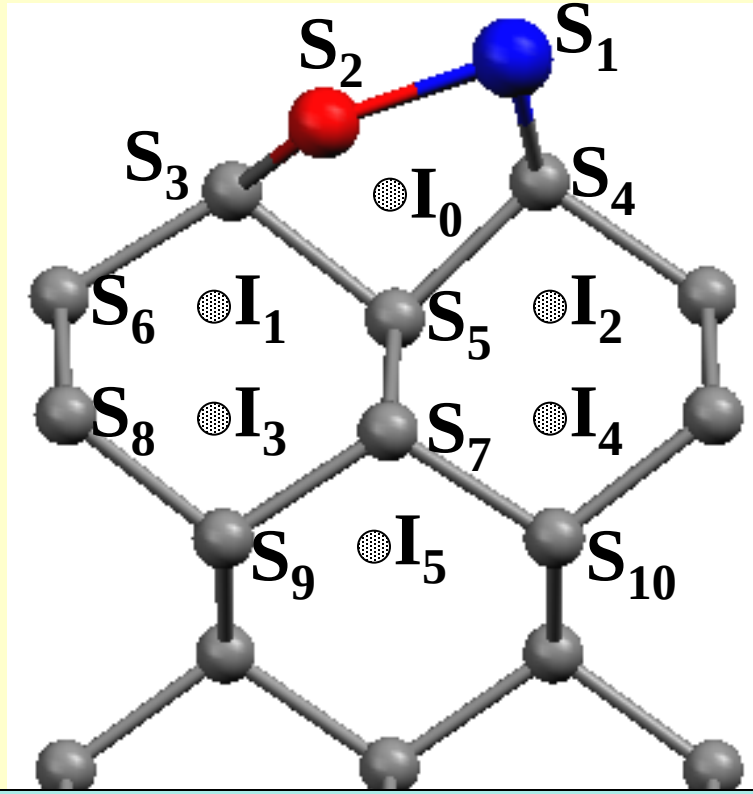
- DFT-GGA calculations
- spin polarized

Side View

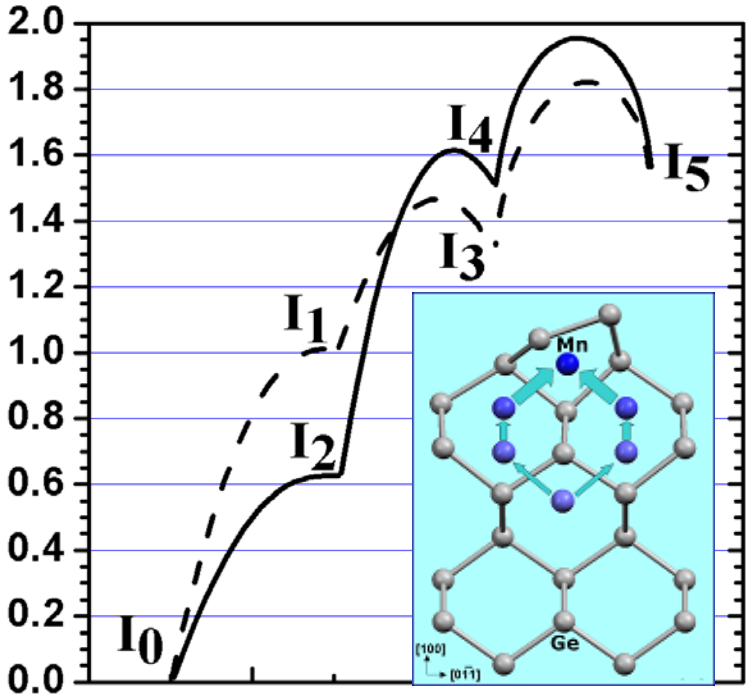


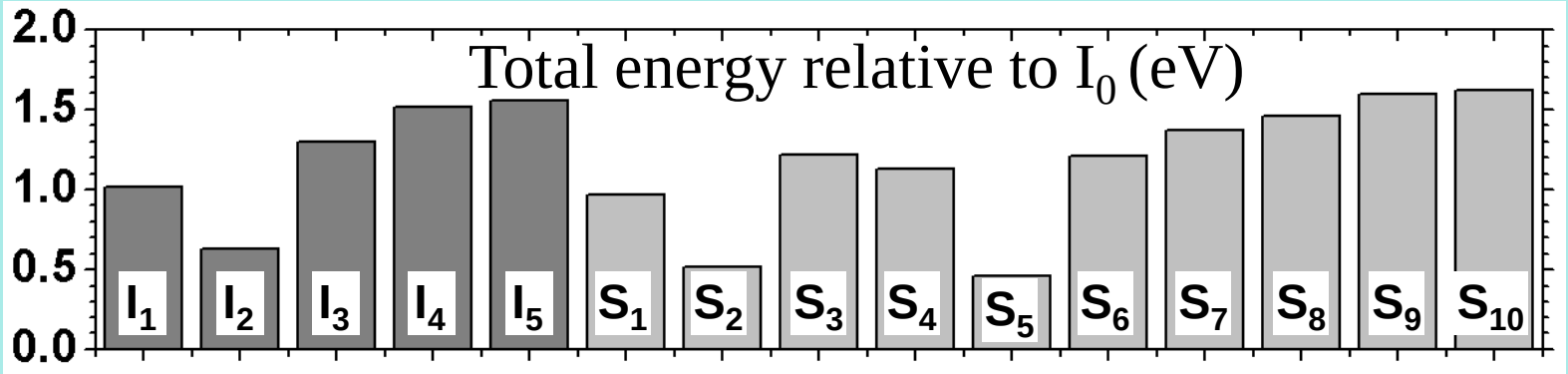


Subsurface segregation of Mn on Ge(100)-2x1

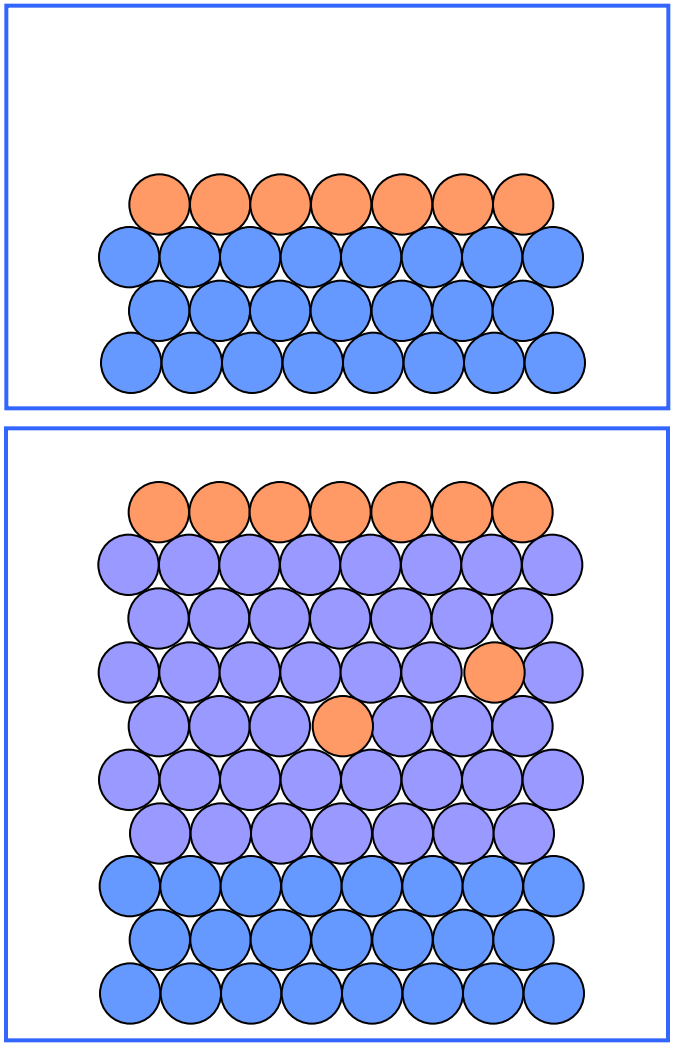


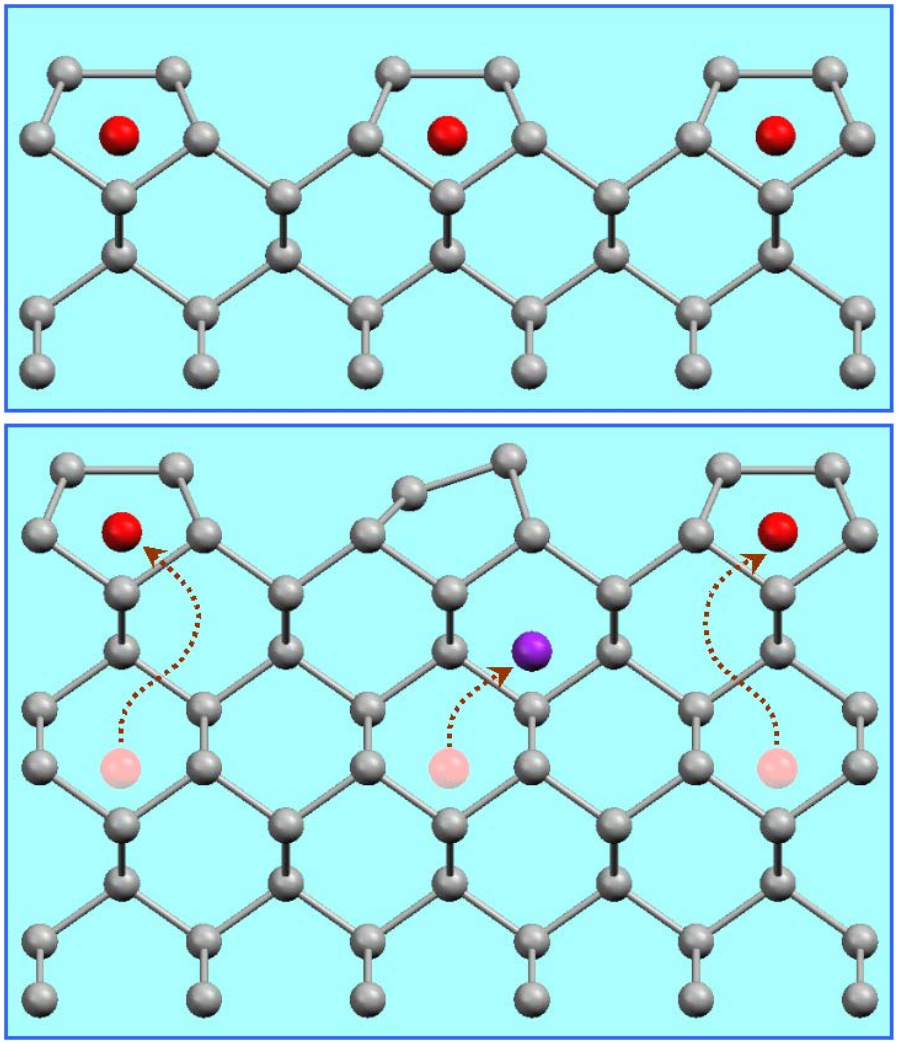
"Subsurfactant Action"





Surfactants vs. Subsurfactants





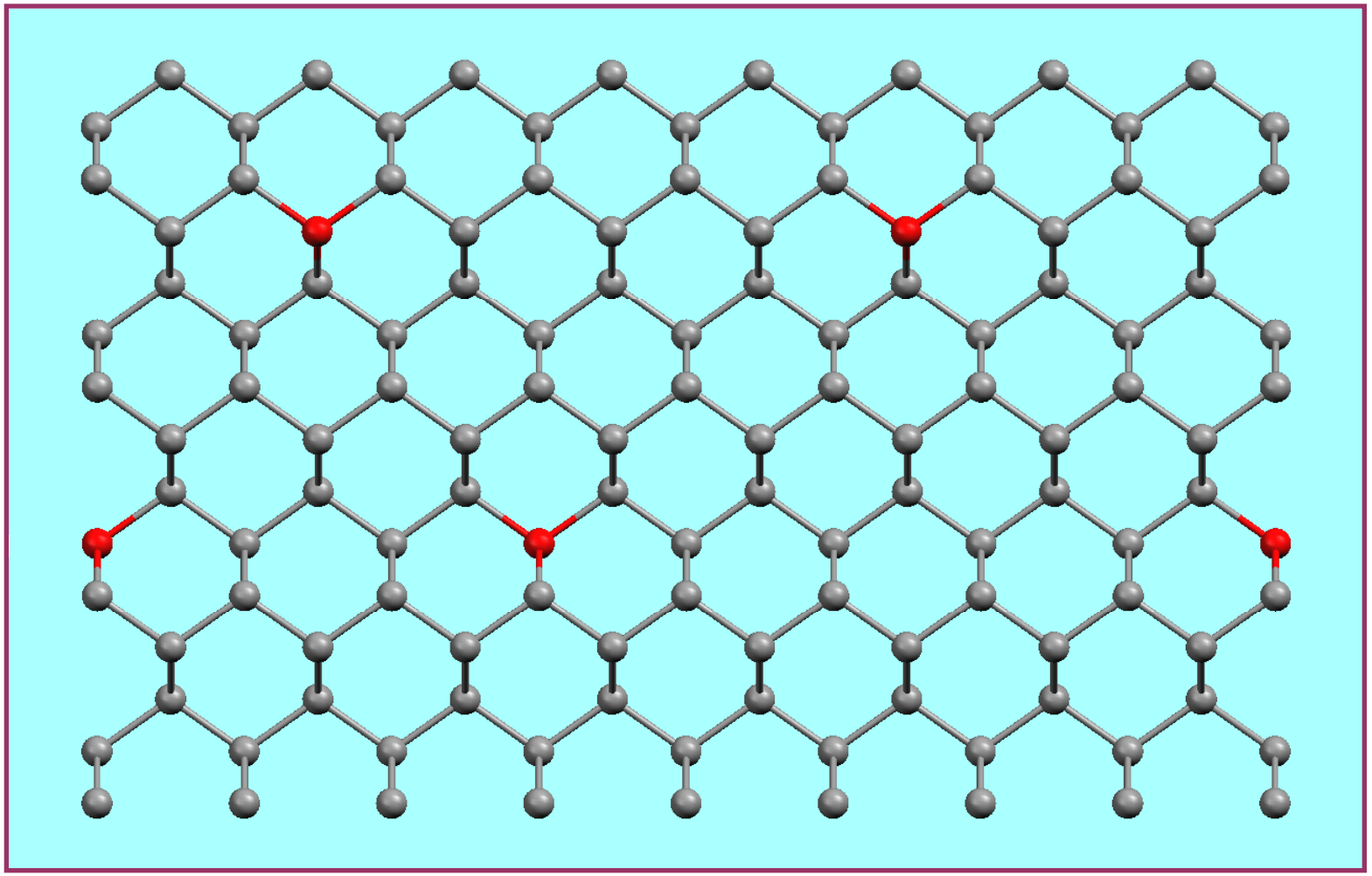
M. Copel, et al., PRL 63, 632 (1989).

W. Zhu, et al., PRL **93**, 126102 (2004).

Trapping: bad

Trapping: good!!!

Doping via Subsurfactant Epitaxy?



Ge

Ge: Mn

Ge

Ge: Mn

Ge

Notable Results on the Theory Side

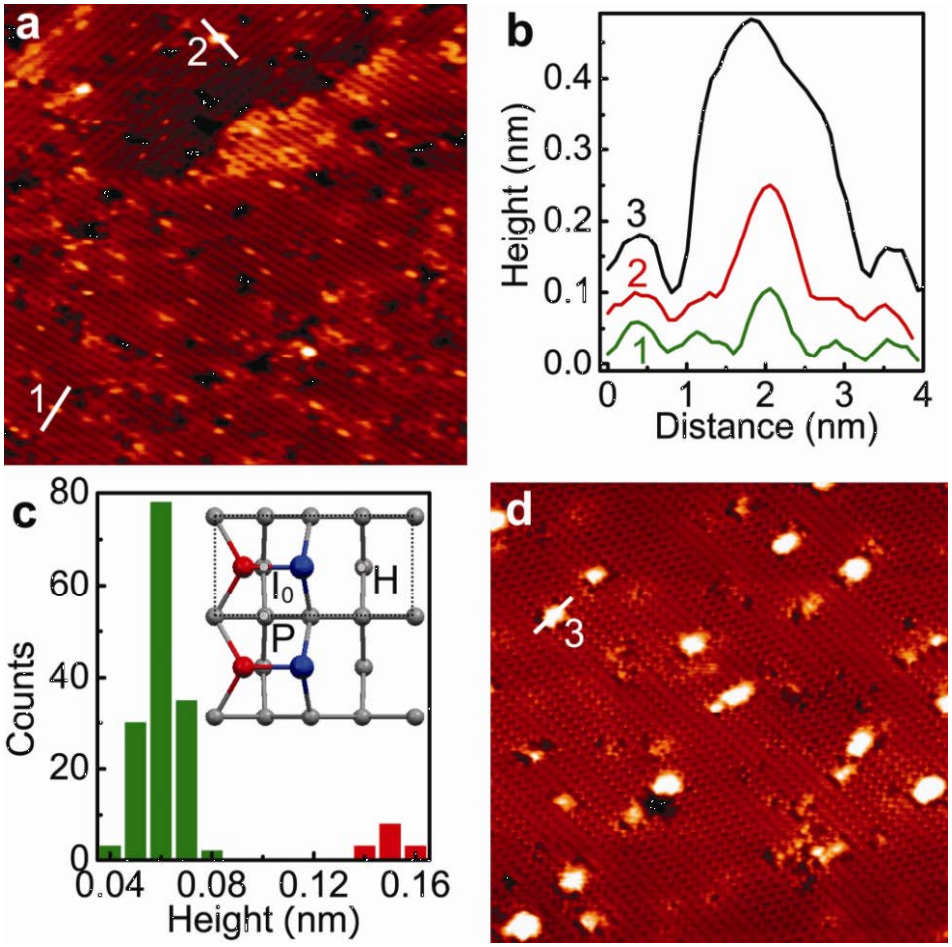
■ On Ge(100), Mn prefers I_0 to substitutional sites, in contrast to bulk Ge, where substitutional sites are preferred.

■ The strong preference of I_0 by Mn is due to local stress associated with Ge-Ge dimerization, whose removal by hydrogen passivation destablizes the I_0 sites.

■ A very different picture on Mn/Ge(111): Mn can easily penetrate into the subsurface sites, then diffuse further inward to become interstitials in the bulk.
Zeng,Zhu, Erwin, Zhang, Weitering, PRB 70, 205340 (2004).

Experimental Confirmation:
Strong preference of Subsurface Sites

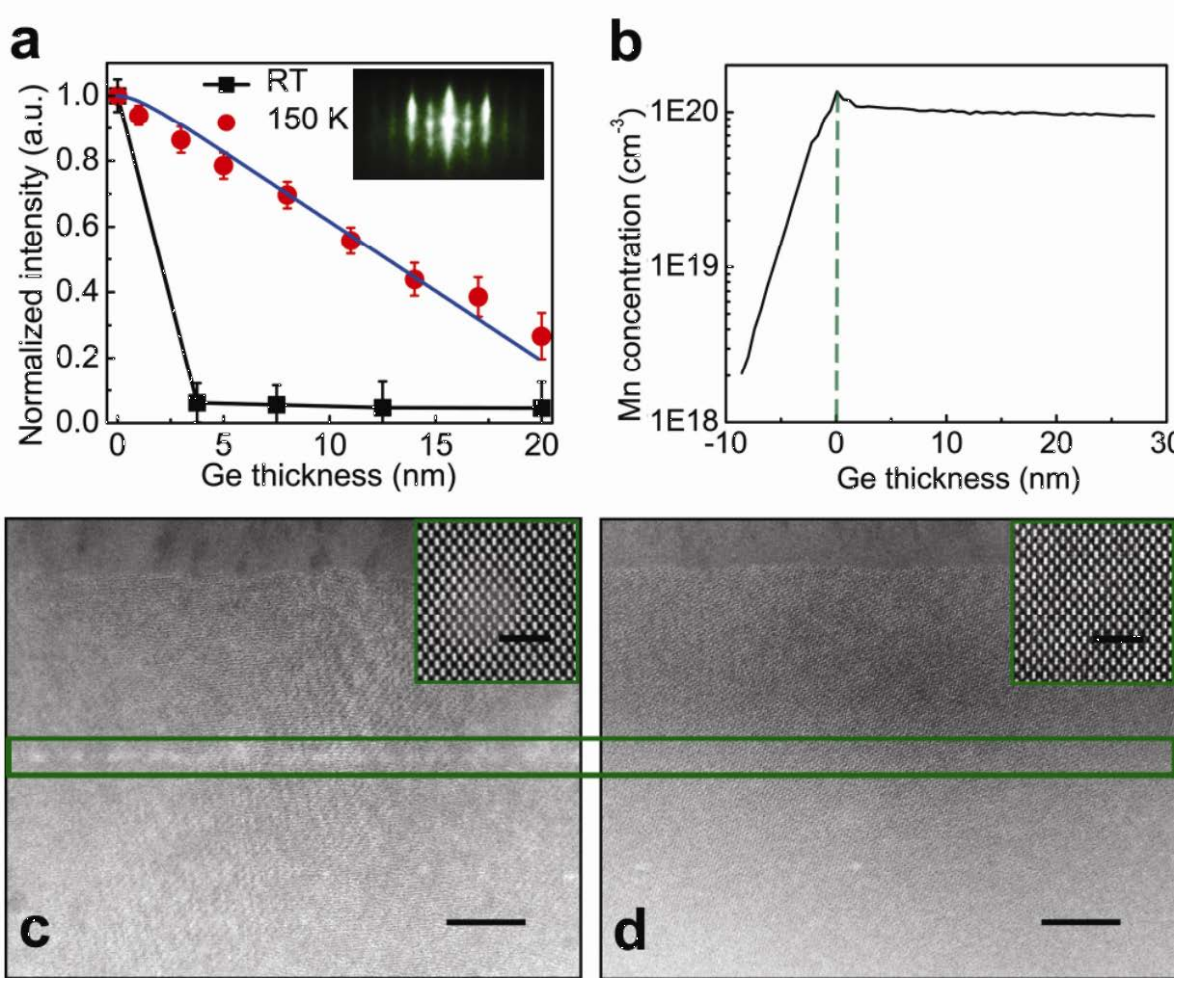
Low T: Scattered



RT: Clustered

Experimental Confirmation:
Floating and doping

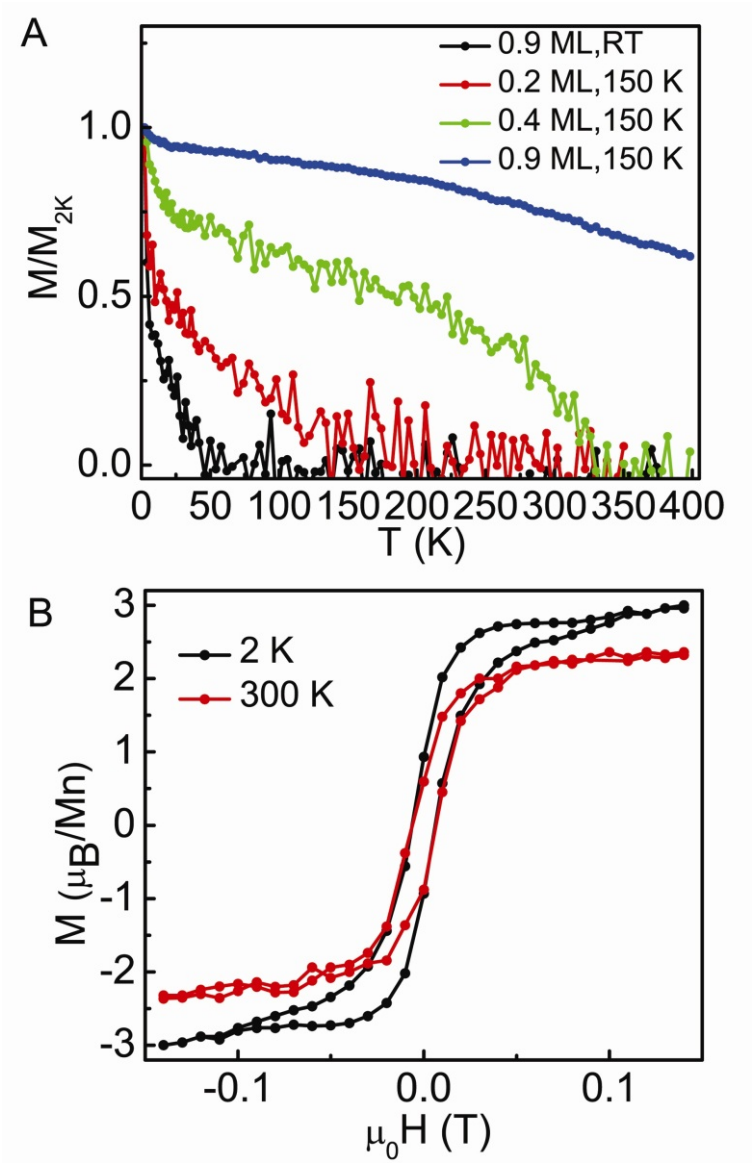
XPS



SIMS

X-STEM

Key Discovery beyond Theoretical Expectation:

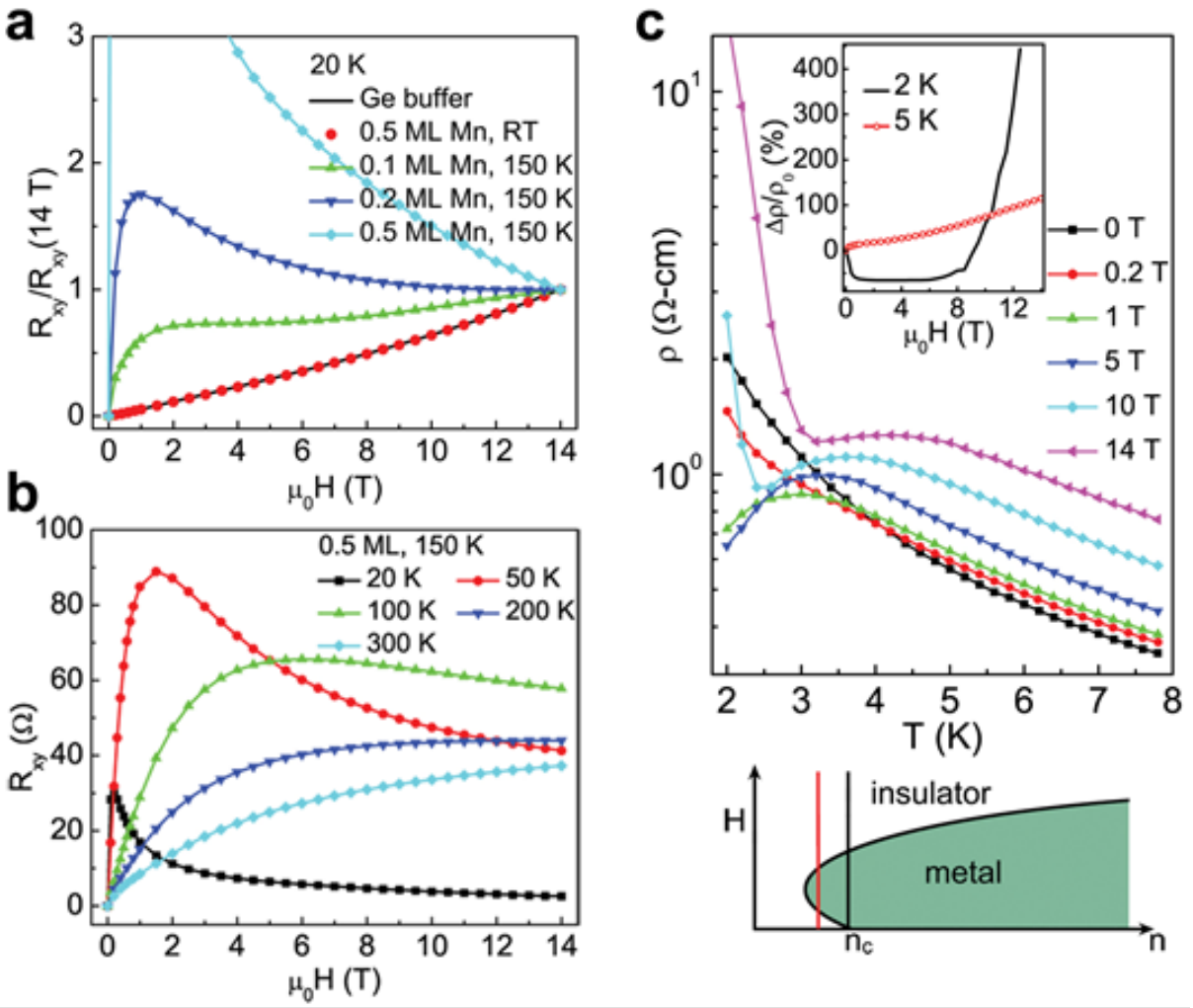


A sweet treat from Mother Nature:

T_c>400K at 0.23% Mn!!!

Transport Properties

- Anomalous Hall Effect (AHE)
- Insulator-Metal-Insulator (IMI) Transitions



Notable Results on the Experiment Side

- Cross checked for unintentional contaminates of every other magnetic element by SIMS, all too low.

- The 0.25% Mn concentration is at or below the ion channeling resolution limit --- A definitive proof of the substitutional doping nature of Mn is still yet to be achieved.

- No subsurfactant epitaxy observed on Ge(111)
Zeng, Zhu, Erwin, Zhang, Weitering, PRB 2004.

Summary on Subsurfactancy

- A novel growth mode, Subsurfactant Epitaxy, has been proposed theoretically and confirmed experimentally.

- Most surprisingly, it offered an optimal way to dope the right amount of Mn into (presumably) the right sites inside Ge, resulting in a striking increase of T_c>400K at the nominal dopant levels of ~0.23%!

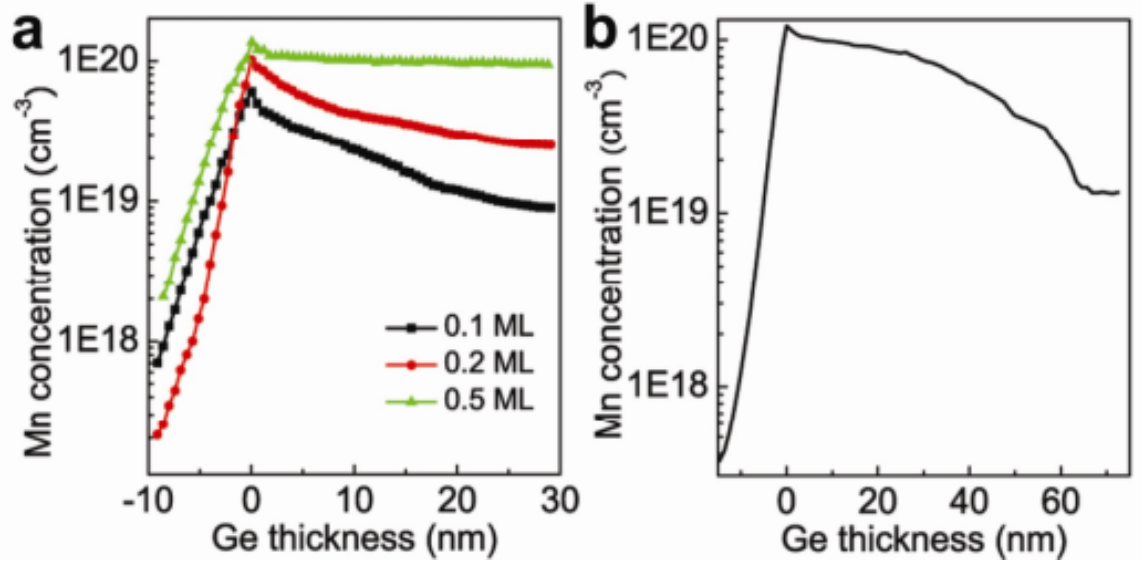
- Subsurfactant Epitaxy should be applicable to other related systems requiring doping levels beyond the thermodynamic solubility limits.

Challenging Open Questions

- **Why constant (0.23%) ?**

  kinetic solubility?

  see: Zhang, S.B. & Wei, S.H. *PRL* **86**, 1789 (2001).



- **Why so low (0.23%), yet so good (T_c>400K) ?**

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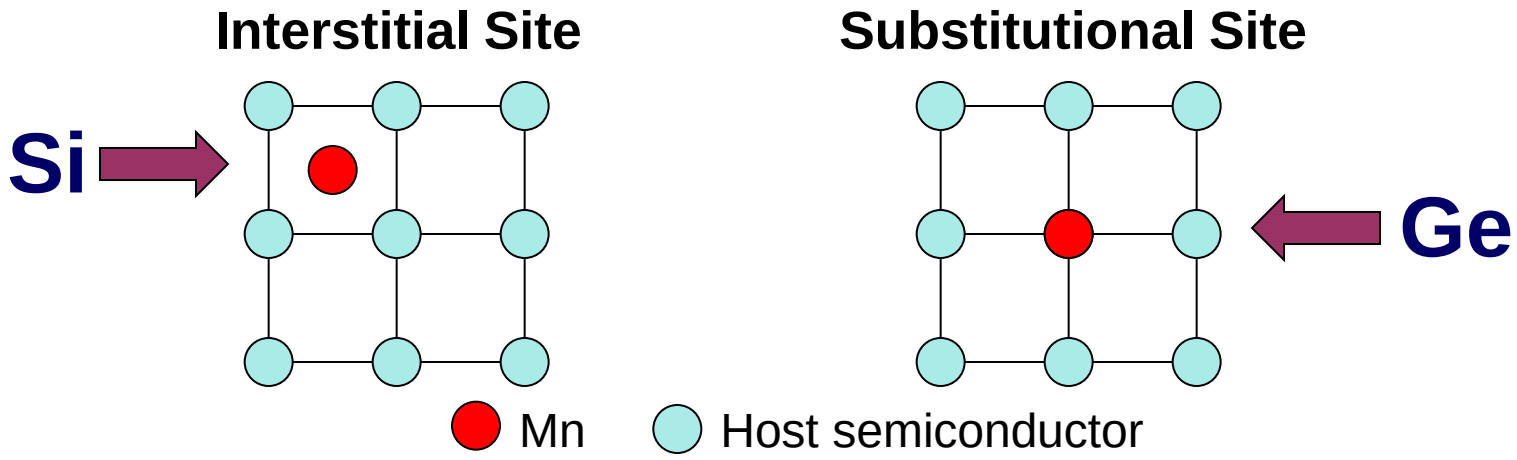
- **Non-Compensated n-p Codoping of DMS Materials**

B. Aided by Conventional Electronic Dopants

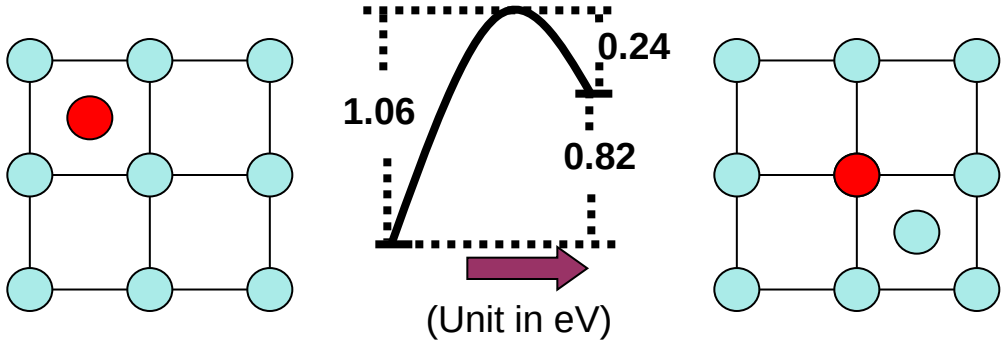
Prediction: Wenguang Zhu, ZZ, E. Kaxiras, PRL (2008)

Also: from DMS to DMO

Preference of Mn in Bulk Si and Ge

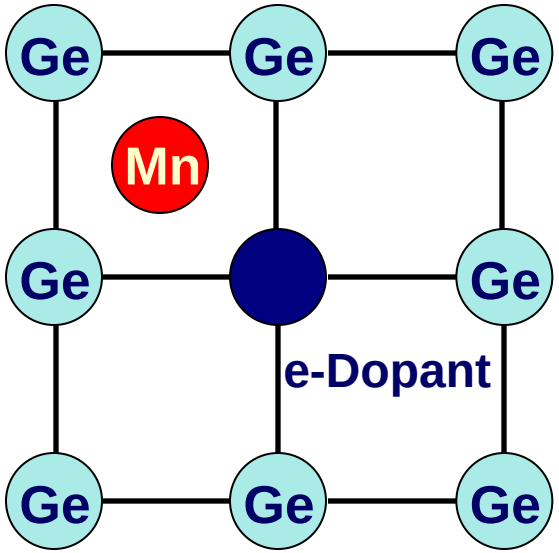


- **In bulk Si, Mn prefers interstitial sites by 0.58 eV.**
- **In bulk Ge, Mn prefers substitutional sites by 0.63 eV, but has to overcome an energy barrier of 1.06 eV to replace a host Ge atom.**



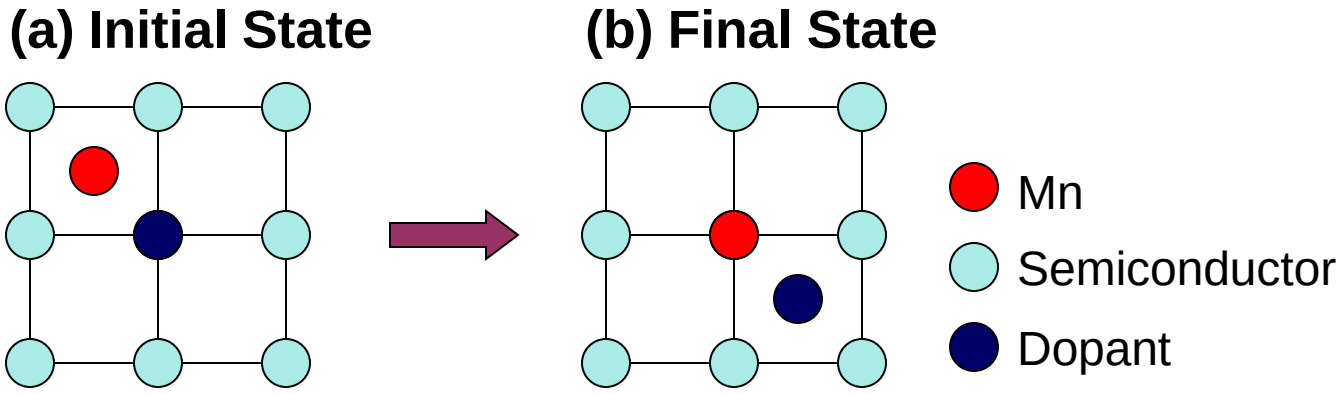
Conjecture: Can An e-Dopant Help?

The assistance of n-type or p-type dopants in the bulk structures might make it easier for the Mn atoms to be incorporated into substitutional sites.



p		n
aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76

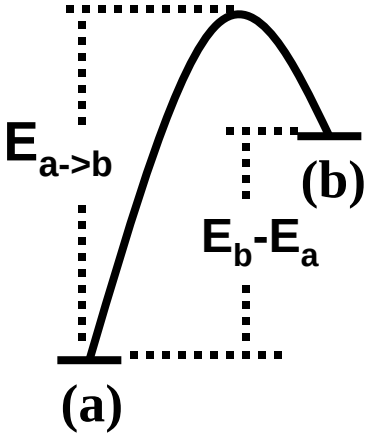
Direct Place Exchange?



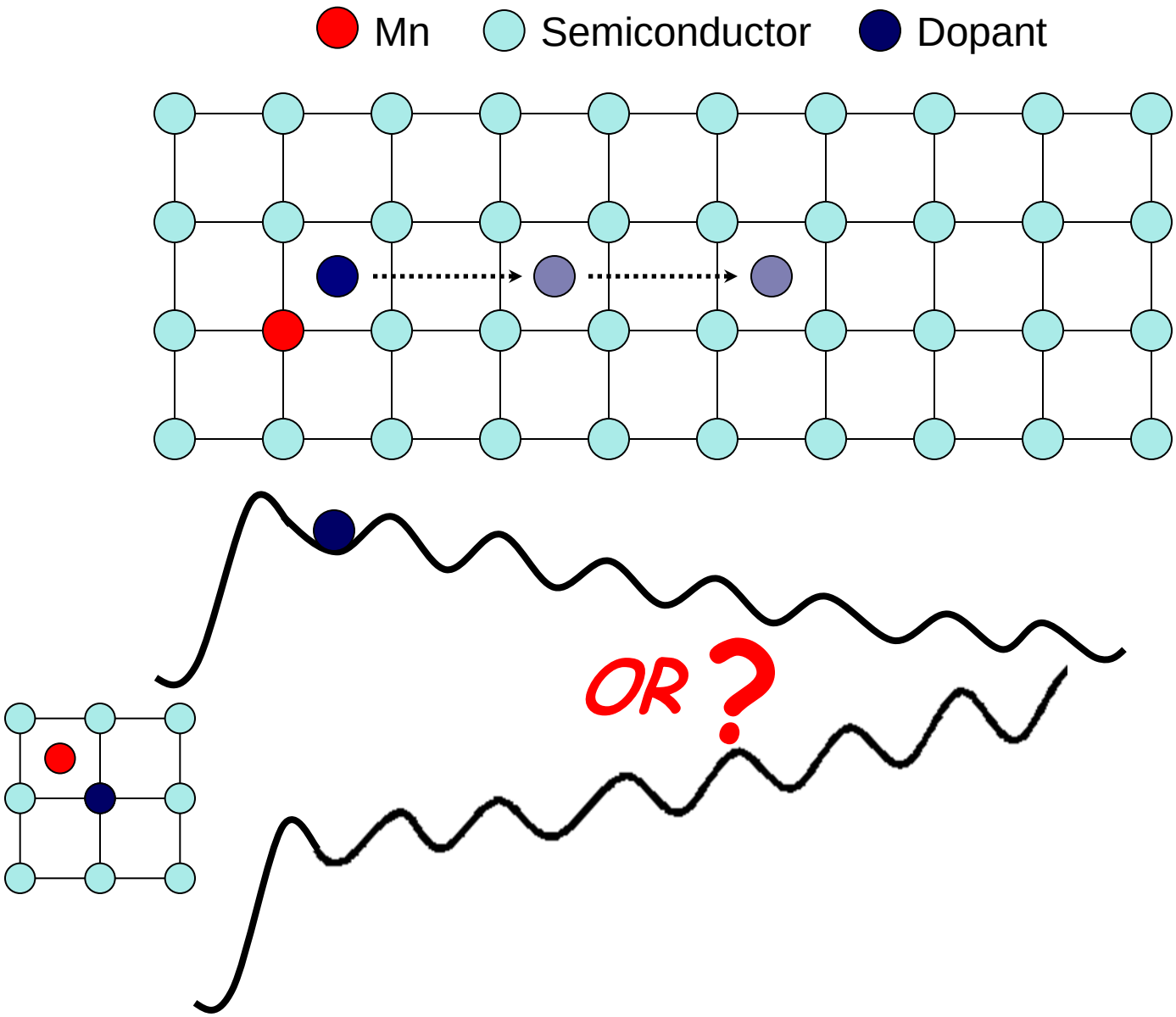
Si		Ge		
Dopant	E_b-E_a	Dopant	E_b-E_a	$\varepsilon_{a\rightarrow b}$
Si	2.03	Ge	0.82	
P	1.46	P	0.33	0.88
As	1.55	As	0.42	0.98
Sb	2.48	Sb	1.42	
Al	1.24	Al	0.94	
Ga	1.79	Ga	1.05	

(Unit in eV)

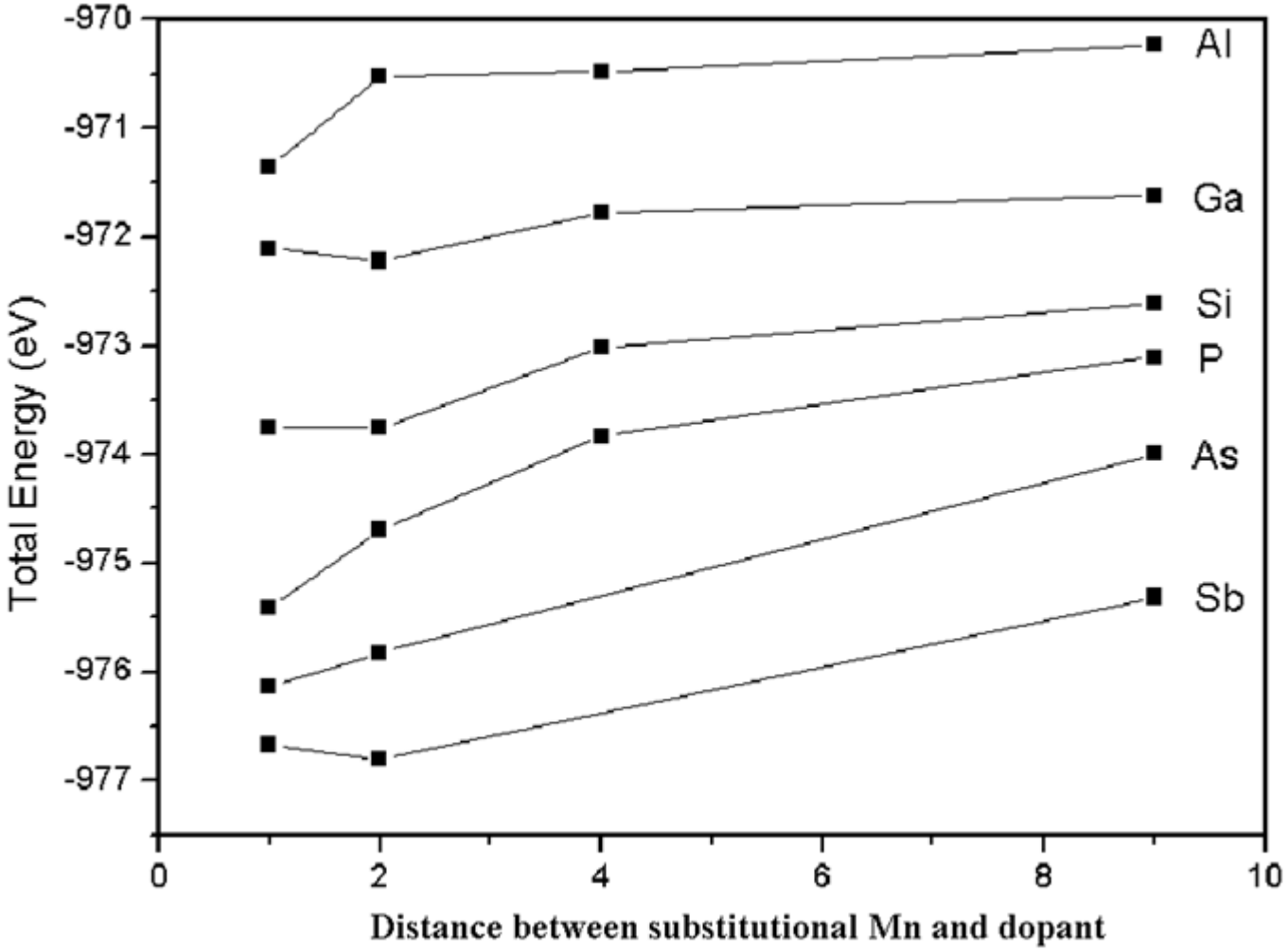
Energy Profile



Is the Final State Stable or not ?



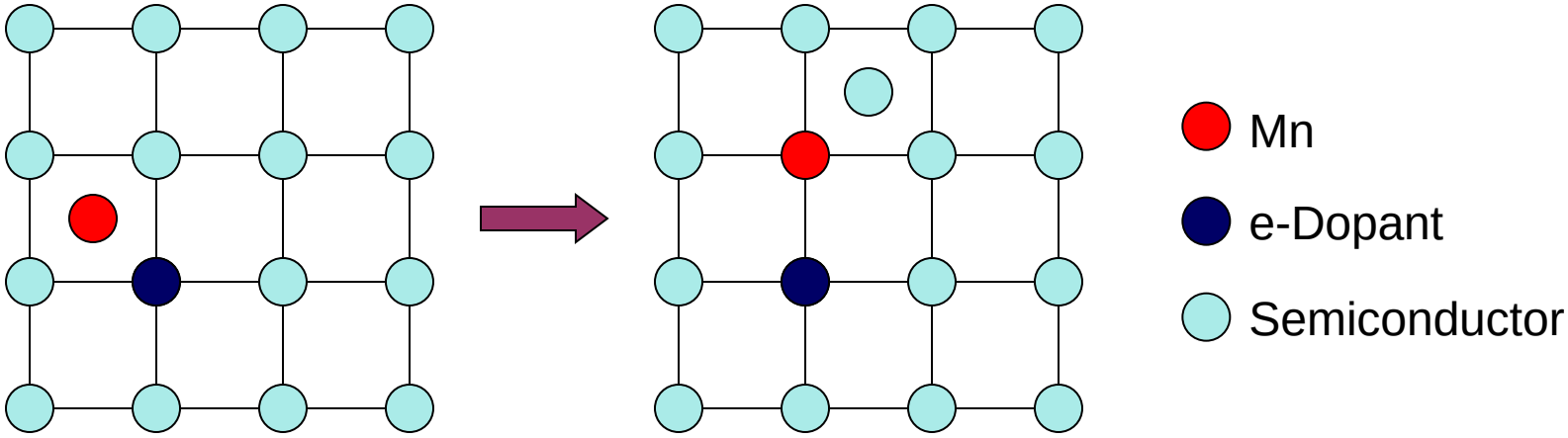
Dopant Can Not Easily Diffuse Away



First try fails !

Mn Substitutional Dopping Aided by n

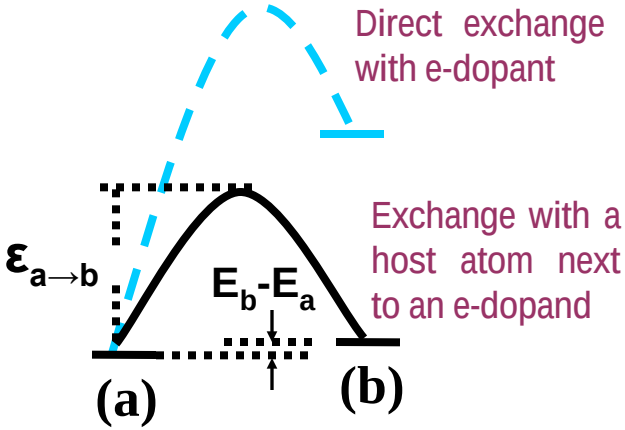
An e-dopant still occupies a substitutional site, while a neighboring interstitial Mn atom exchanges with a host semiconducting atom.



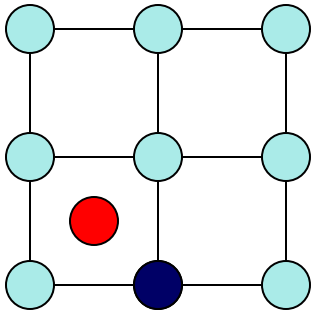
Si		Ge		
Dopant	**E_b-E_a**	**Dopant**	**E_b-E_a**	**$\varepsilon_{a\to b}$**
Si	2.03	Ge	0.82	
P	0.89	P	0.03	0.34
As	1.09	As	0.05	0.25
Sb	1.27	Sb	0.22	0.38
Al	2.05	Al	1.54	
Ga	2.43	Ga	1.52	

(Unit in eV)

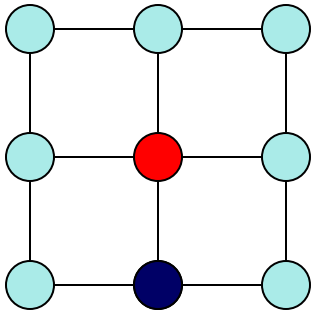
Energy Profile



Formation Energy of a Mn / e-dopant Substitutional Pair



(a)



(b)

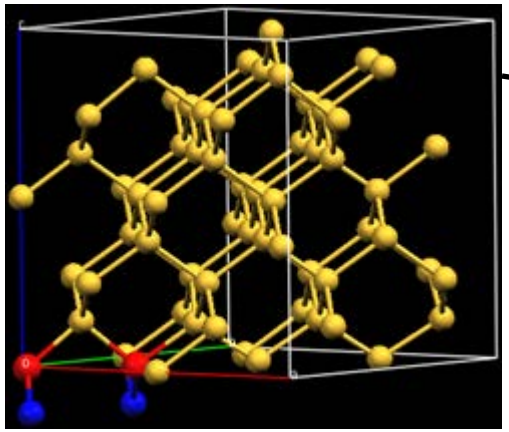
	Relative formation energy: $(E_b+\mu_{host}) - E_a$			
	P	As	Sb	Undoped
Si	-0.84	-0.87	-0.81	+0.58
Ge	-1.35	-1.42	-1.42	-0.63

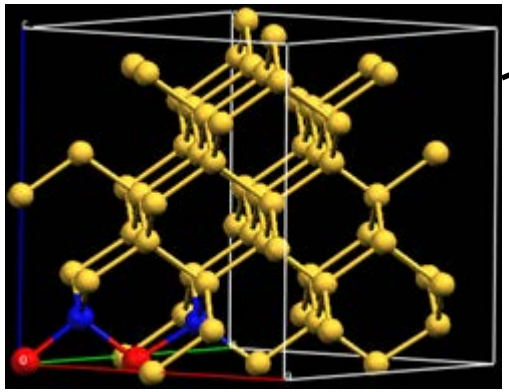
(Unit in eV)

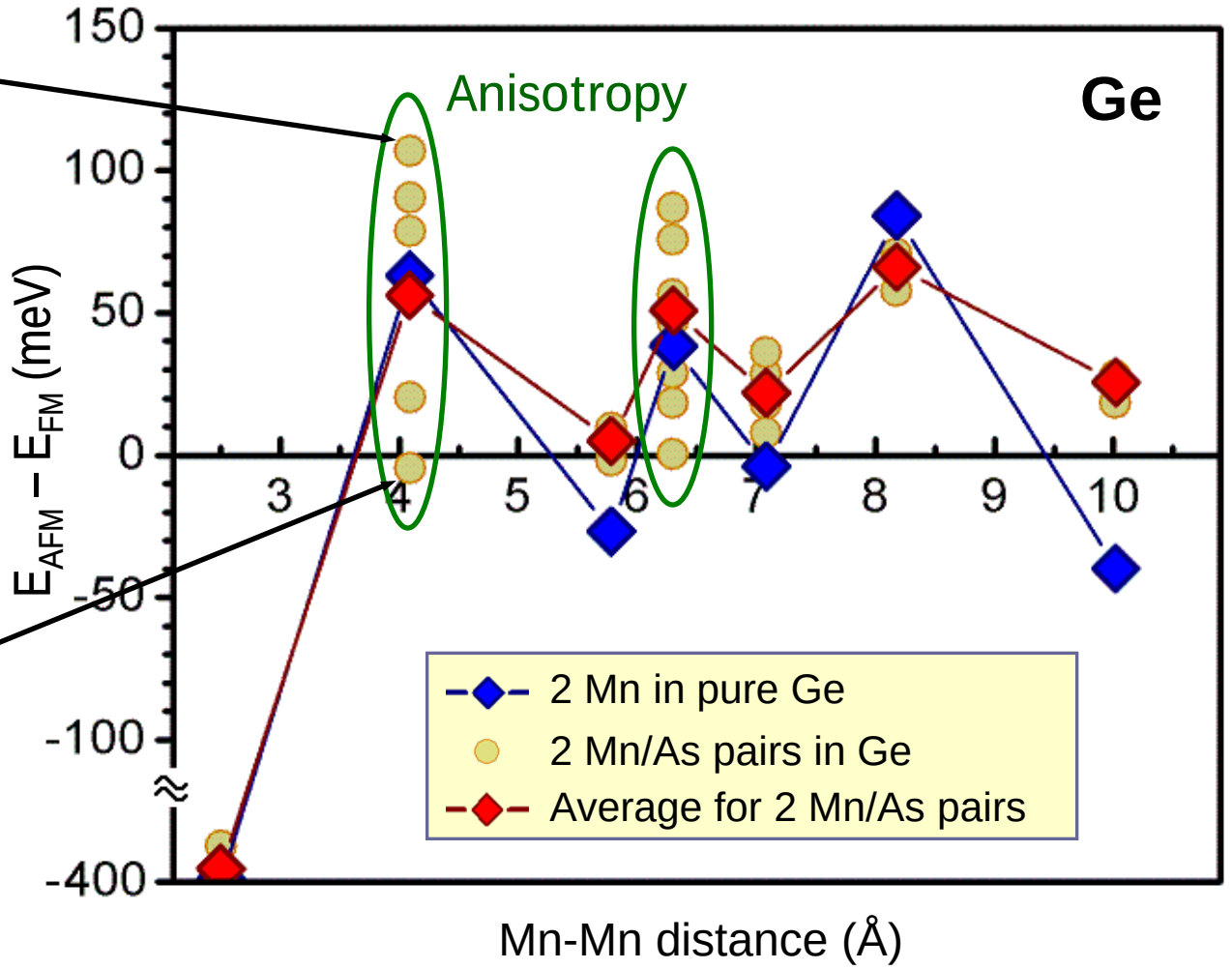
p-type Substitutional Mn → ← n-type e-dopant

Coulomb attraction

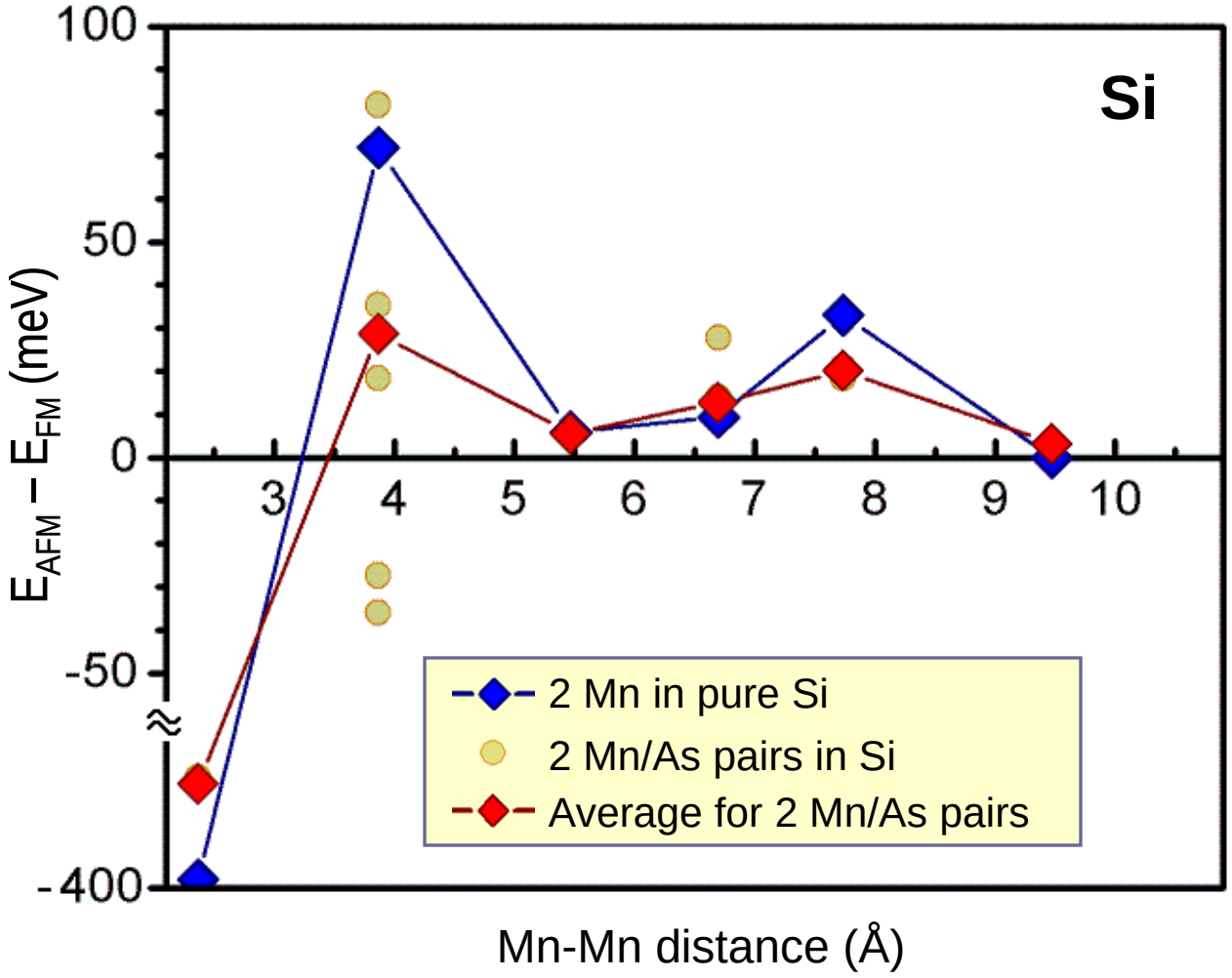
Strongly Anisotropy in Magnetic Coupling Between two Mn/e-dopant Pairs







Strongly Anisotropy in Magnetic Coupling Between two Mn/e-dopant Pairs



Some Questions and Ongoing Efforts

■ Even for Mn doped into Ge, Mn-Mn coupling along a given direction is non-oscillatory.

See: Zhao, Shishidou, Freeman, PRL 2003.
Hamadevan, Sarma, Zunger, PRL 2004.

■ Mn: double or triple acceptor; e-dopant: single acceptor. Reason for surviving magnetic coupling?

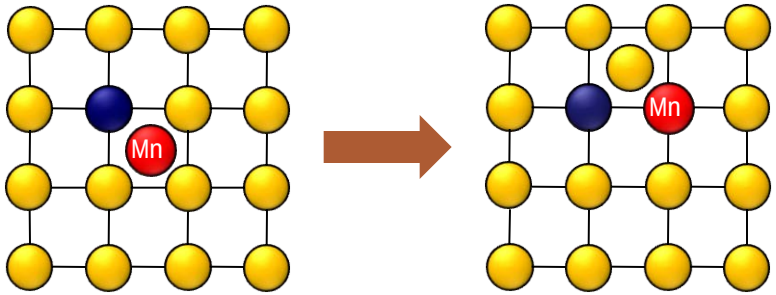
■ VASP: Ge is metallic.
LDA+U?
GW?

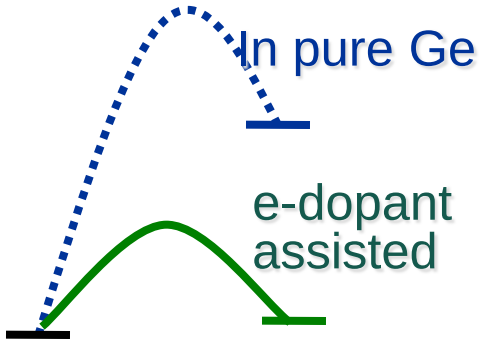
■ From structures to transport?
Hong Guo

Summary on non-compensated p-n codoping

- A novel kinetic process is proposed to incorporate Mn into the host lattice of bulk Ge with the assistance of an adjacent conventional n-type electronic dopant.
- The Mn/e-dopant substitutional pair is thermodynamically favorable in both Si and Ge.
- Two Mn/e-dopant pairs always favors ferromagnetic couping in Ge and Si except at the nearest Mn-Mn distance.
- The magnetic coupling between two Mn/e-dopant pairs exhibits strong anisotropy at some distances in both Si and Ge.

Physical Foundation & DFT Validation





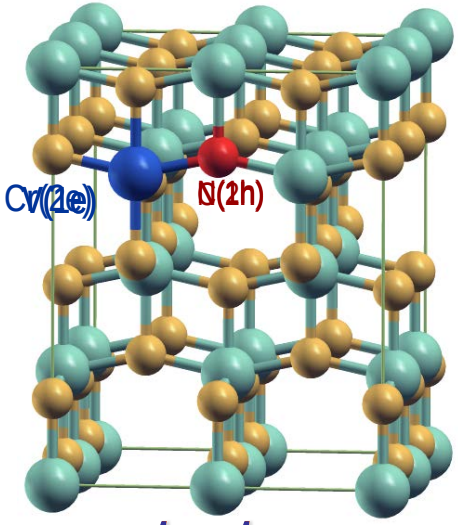
Substitutional Mn (+2 or +3) ⟷ ***n*-type e-dopant (-1)**

Coulomb attraction

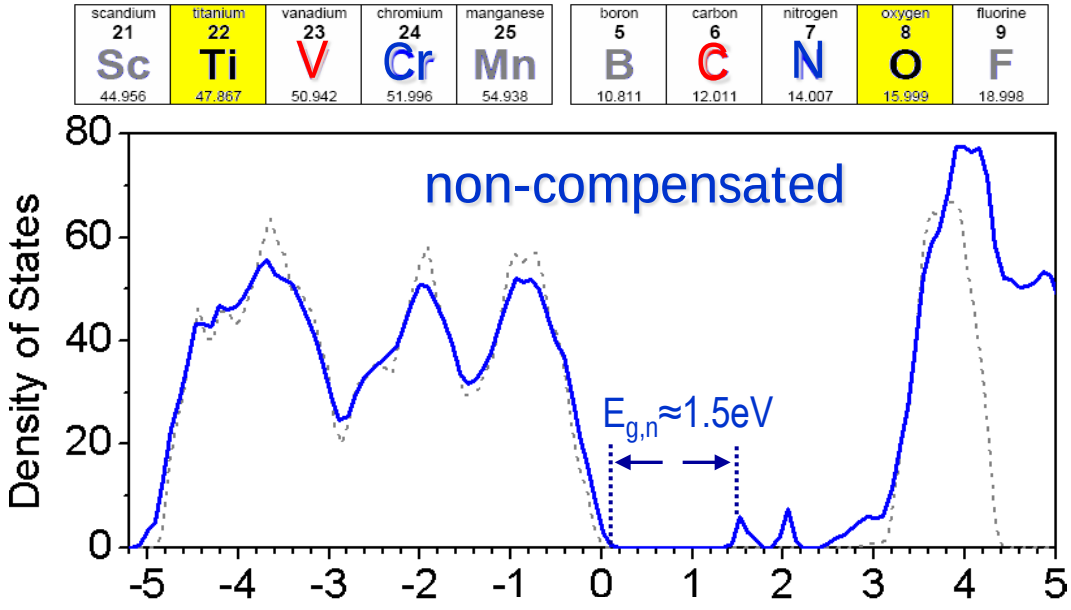
Mn_xGe_{1-x} as DMS
Zhu, Zhang & Kaxiras
PRL 2008.

See also:
Mn in III-V as DMS
Dietl et al.
Nature Materials 2007.

Anatase TiO_2



net p-type



Looking Forward

■ Will the favoring of FM order and the enhanced magnetic anisotropy translate into higher Tc?

■ Experimental confirmations (perhaps back to co-deposition by MBE)?

■ Any connection between the two parts (especially the magnetic properties)?

Monte Carlo study of the Curie temperature of Mn/As co-doped Ge

Ref: H. Chen, W. G. Zhu, E. Kaxiras, and ZZ, PRB 79, 235203 (2009)

Model Hamiltonian: Classical Heisenberg Model

$$H = -\sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$$

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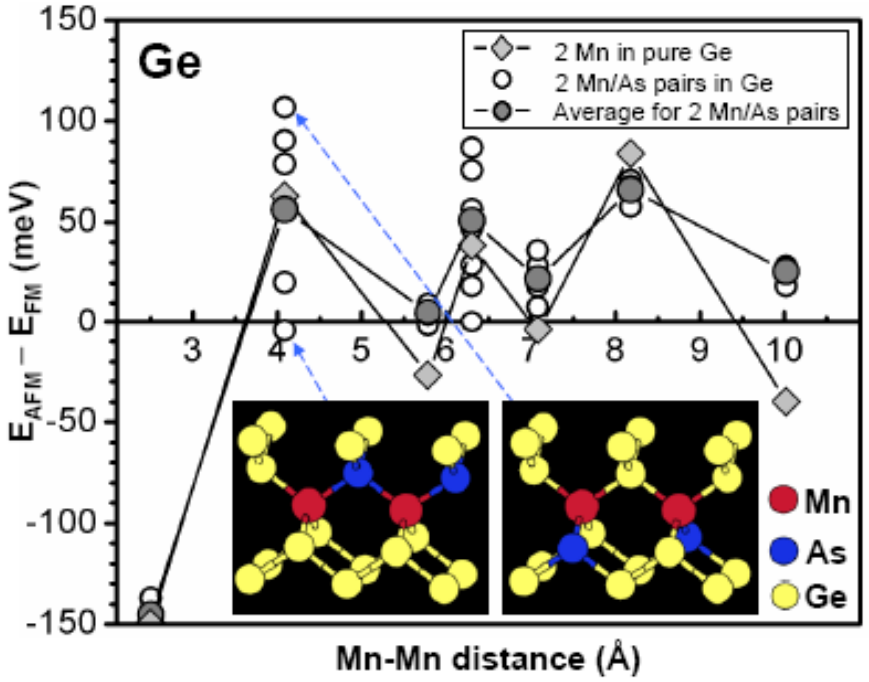
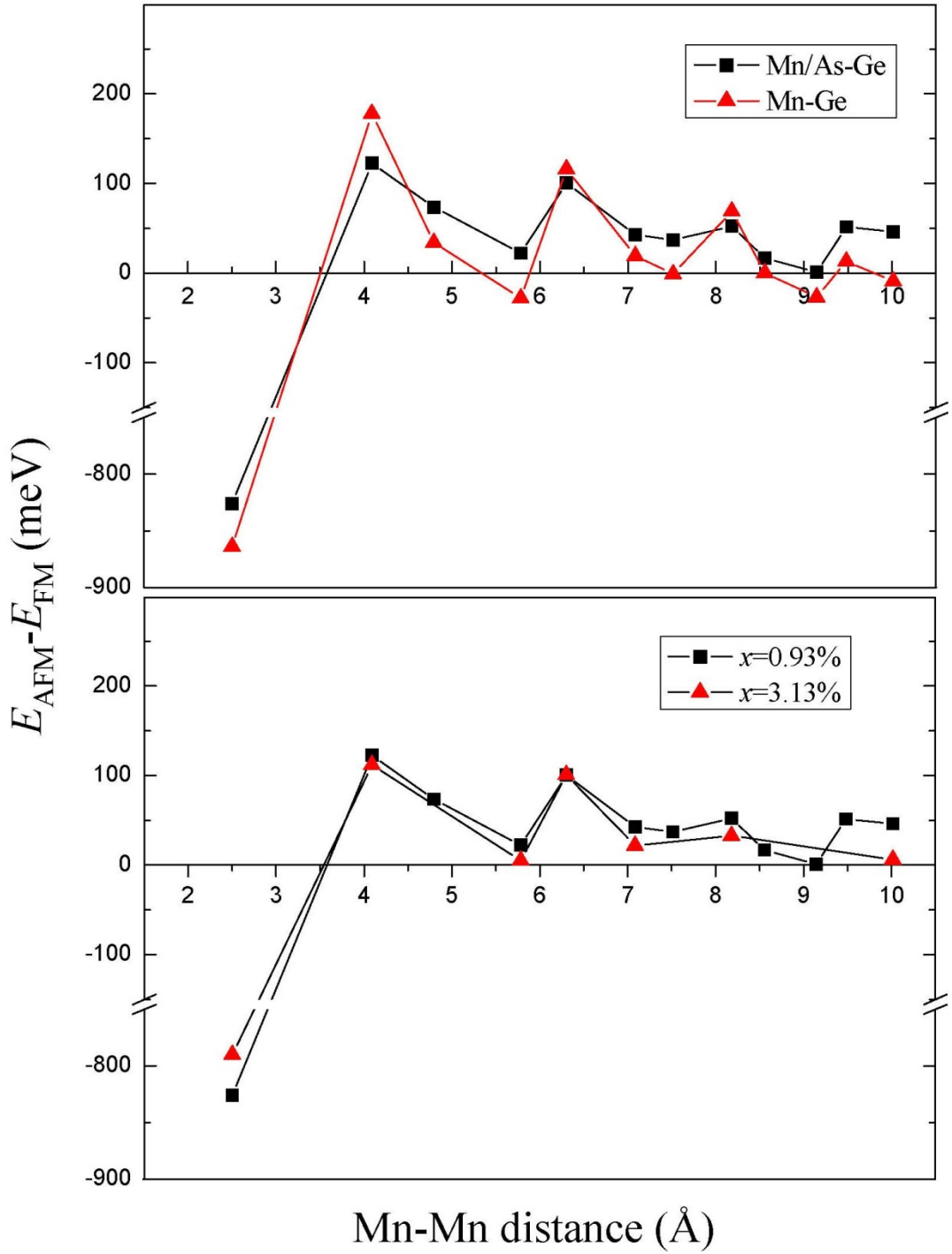
Curie temperature: A Two-Step Approach

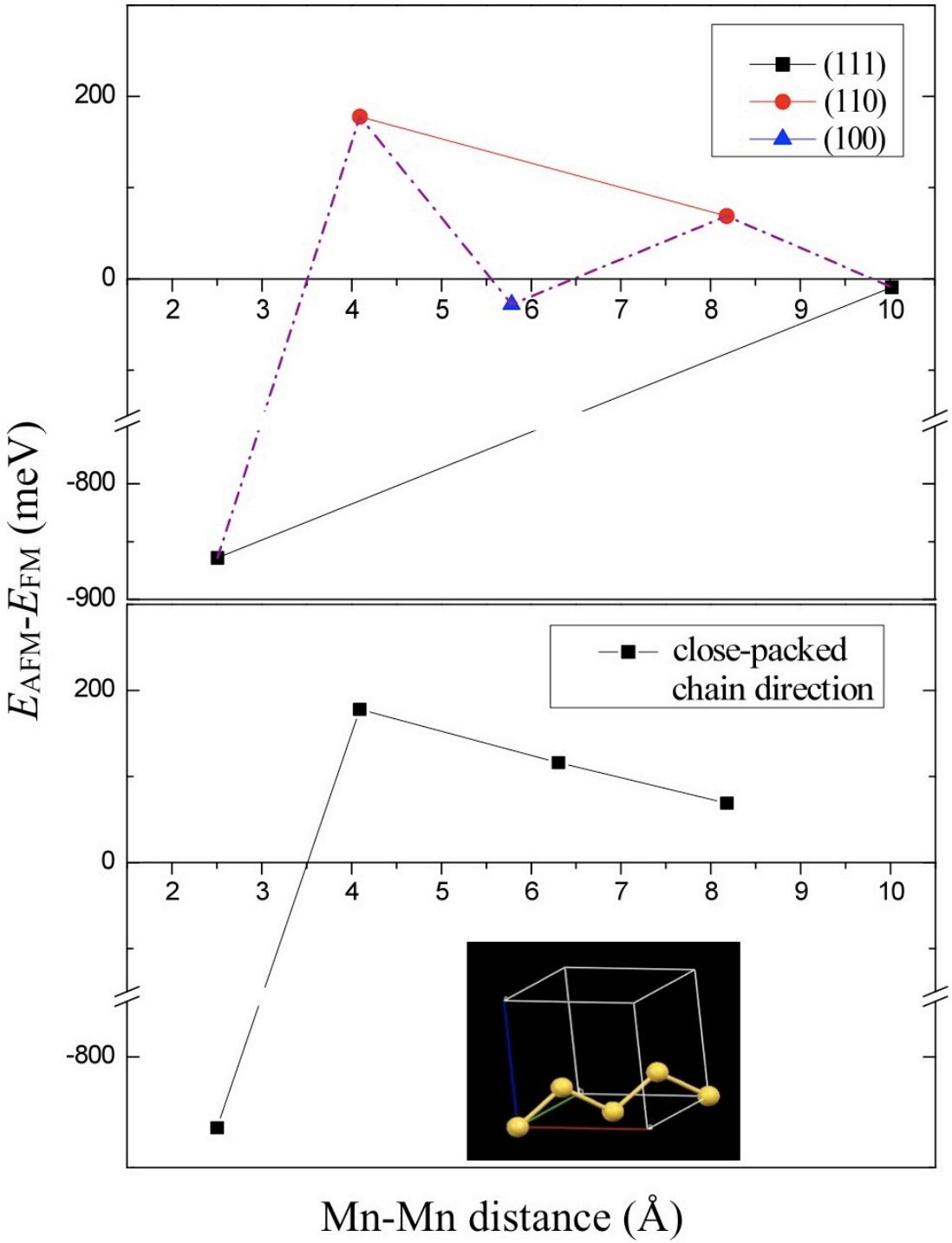
- 1. Exchange interaction constants are determined from supercell *ab initio* calculations.
- 2. Curie temperature is determined by Monte Carlo simulation, using the interaction parameters calculated in 1.

Determine Interaction Parameters



- Total energy difference between AFM and FM states versus Mn-Mn separation at 3.13% Mn concentration in bulk Ge with only two Mn impurities (diamonds),or with two Mn/As pairs (empty circles)


Mn/As-Ge
Mn-Ge
x=0.93%
x=3.13%
200
100
0
-100
-800
-900
2
3
4
5
6
7
8
9
10
E_{AFM}-E_{FM} (meV)
Mn-Mn distance (Å)


(111)
(110)
(100)
200
0
-800
-900
2
3
4
5
6
7
8
9
10
close-packed
chain direction
E_{AFM}-E_{FM} (meV)
Mn-Mn distance (Å)

Curie temperature

- Metropolis algorithm

- 4^{th}-order cumulant crossing method to determine T_c

Binder and D. W. Heermann, *Monte Carlo Simulation in Statistical physics* (Springer, Berlin, 2002).

Curie temperature (contd.)

- Metropolis algorithm:
  - 1.Choose one spin i randomly
  - 2.Generate a random final spin direction of i.
  - 3.Calculate total energy change ΔE after flipping the spin. If ΔE<0, flip the spin, otherwise do the flipping with a probability:

$$p = e^{-\frac{\Delta E}{k_B T}}$$

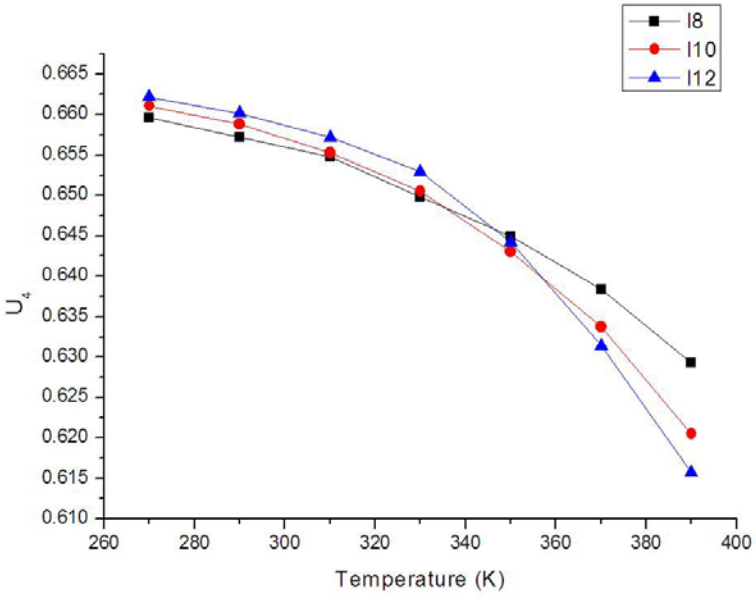
  - Go to step 1

Curie temperature (contd.)

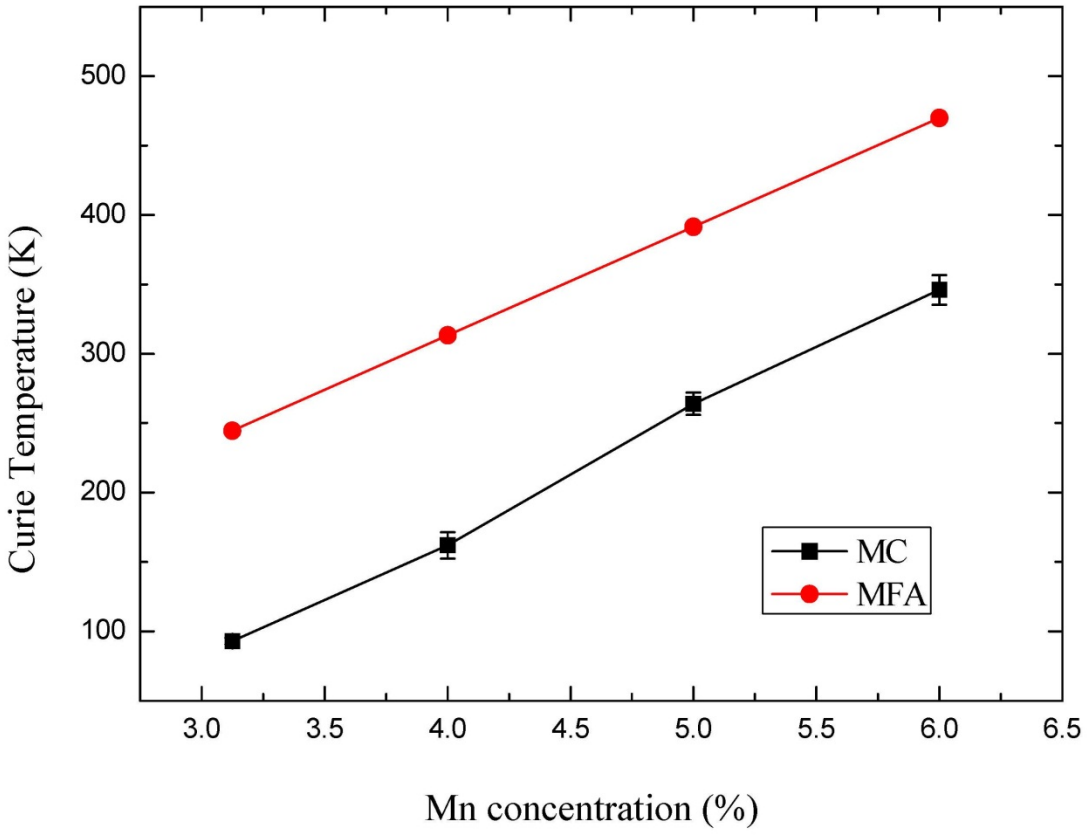
- Ideally, below T_c, U_4 is strictly equal to 2/3, and above T_c, U_4 decays as T^{-1}.

$$U_4 = 1 - \frac{\langle M^4 \rangle}{3\langle M^2 \rangle^2}$$

- T_c can be determined by the crossing of U_4 (T) curves of different supercell sizes.



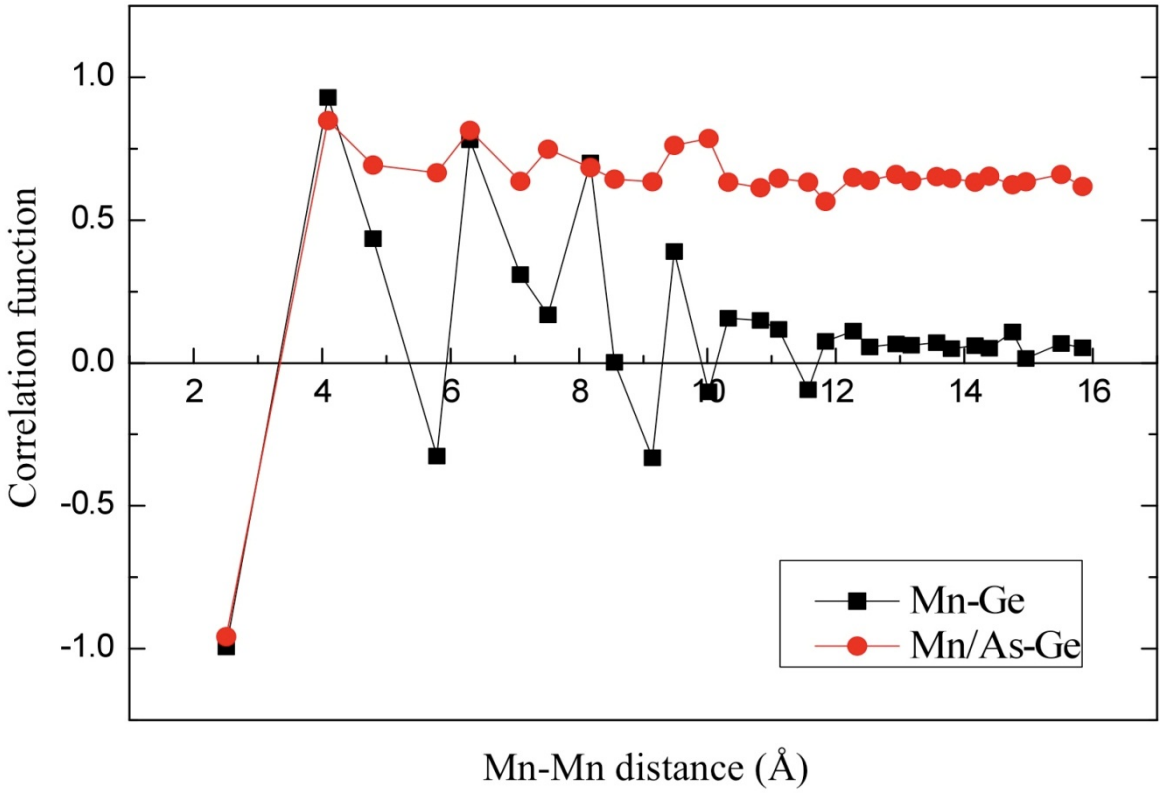
Tc from MC: linear with concentration



1. Coupling parameters by us do not depend on concentration
2. 3% is still higher than the percolation threshold of this system.

Spin-glass behavior of MnGe

Correlation function at T=0.01K



A similar cumulant crossing approach yield a spin-glass phase transition temperature of ~5K for 5% Mn

Concluding Remarks

- Mn in pure Ge: spin glass, very low Tc.
- Non-compensated n-p (Mn-As) codoping: high Tc.
- It is still possible to get homogeneous high-Tc DMS in Mn_xGe_{1-x}.