

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-

???

PARA

SEMICONDUCTORS
1998-

SPIN-FET
Q-BITS

AMR
GMR
TMR

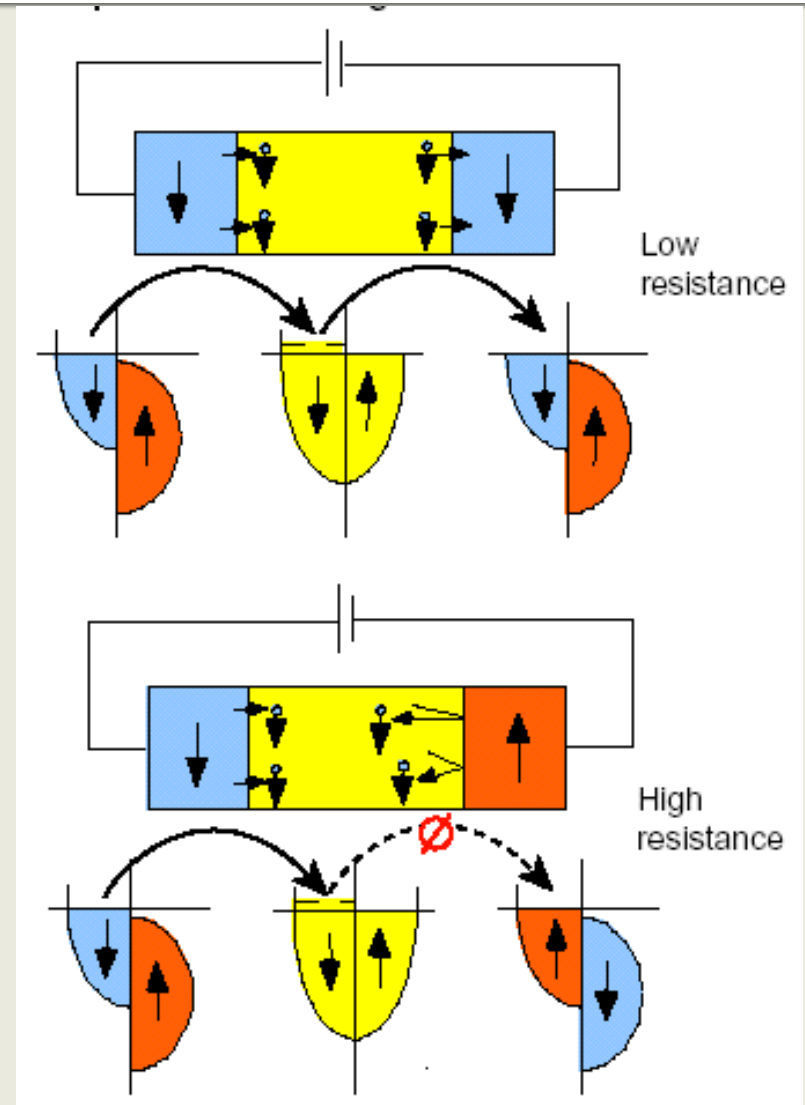
FERRO
(Collective)

AMR
GMR
TMR
+++

Spin-polarized device principles (metallic layers):

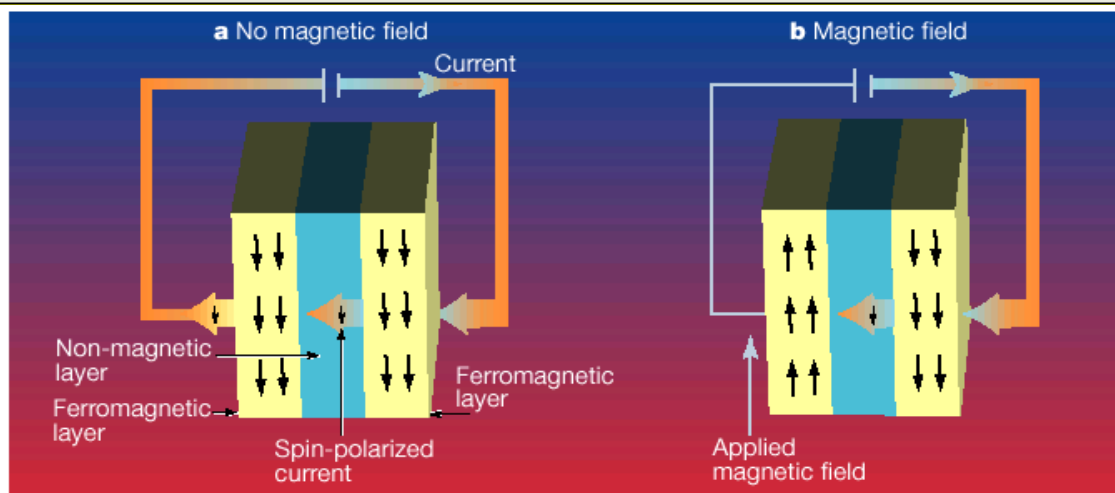
Parallel magnetic layers
 \Rightarrow \downarrow spins can flow

Antiparallel magnetic layers
 \Rightarrow \downarrow spins cannot flow



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

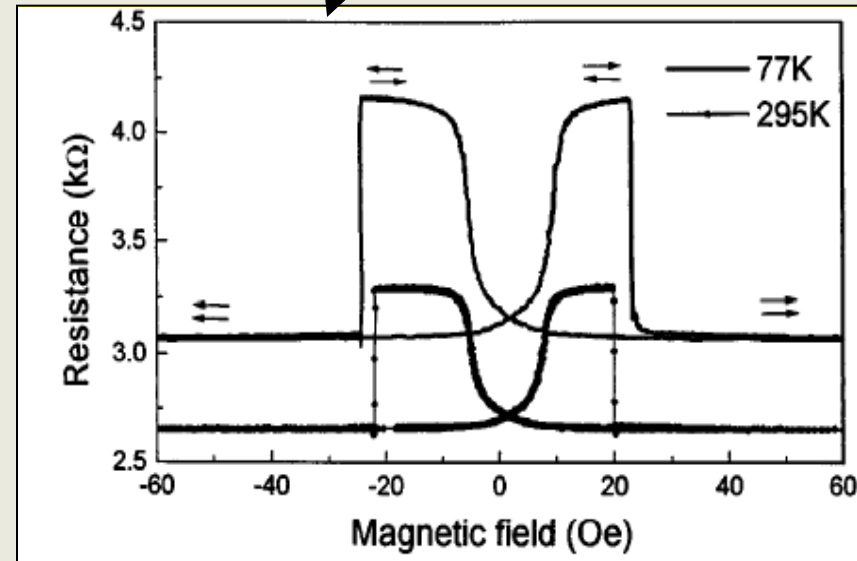
FERROMAGNETIC METALS



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.

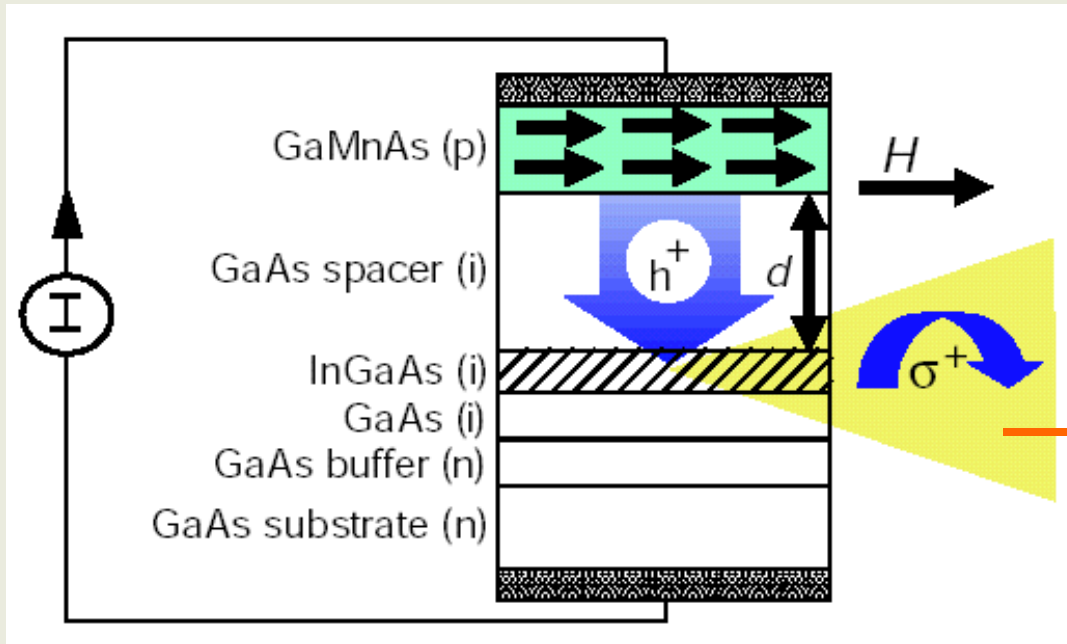
Spin valve GMR

Ferro-Insulator-Ferro TMR



Spin injection into a FM semiconductor heterostructure

Spin transfer

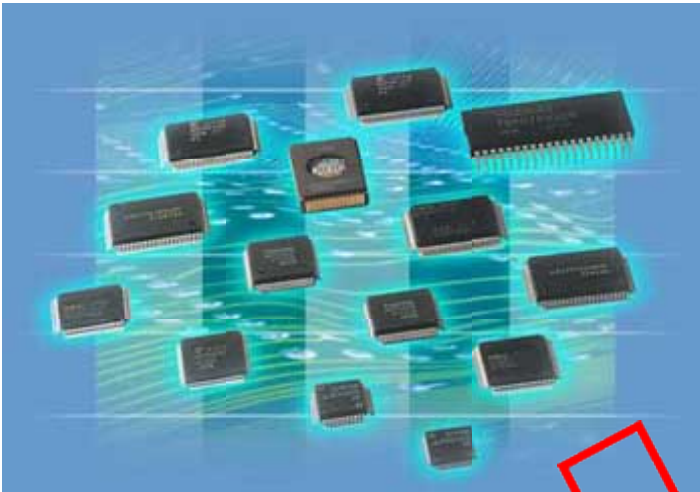


Polarization of emitted electroluminescence determines spin polarization of injected holes

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

Malajovich et al., Nature 2001

Dream Technology Integration



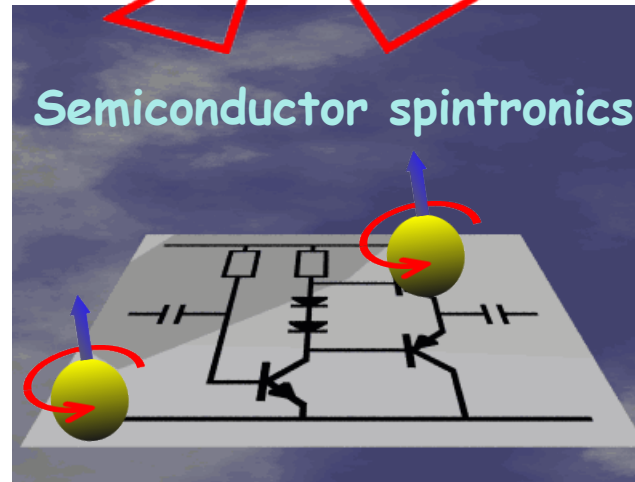
Silicon era



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



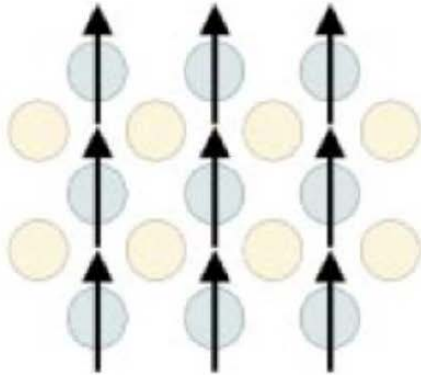
- smaller
- faster
- low power
- non-volatile
- multi-functionality

Outline

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

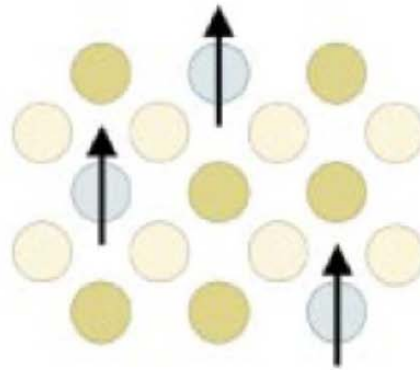
Making semiconductor magnetic: Doping

A



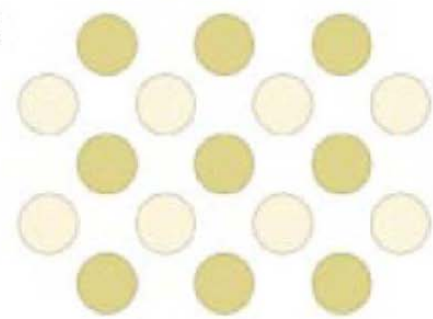
EuS
CuCr₂Se₄
...

B



diluted magnetic
semiconductors

C



Si
III-V
II-VI
...

Magnetic ion: Mn

PERIODIC TABLE
Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs

speed of light in vacuum	c	299 792 458	m s ⁻¹	(exact)
Planck constant	h	6.626 070 15 × 10 ⁻³⁴	J s	($h = h/2\pi$)
elementary charge	e	1.602 176 634 × 10 ⁻¹⁹	C	
electron mass	m_e	9.109 383 56 × 10 ⁻³¹	kg	
proton mass	m_p	1.672 621 9 × 10 ⁻²⁷	kg	
fine-structure constant	α	1/137.035 999 084		
Rydberg constant	R_∞	10 973 731.762 178	m ⁻¹	
	$R_\infty c$	3.289 841 96 × 10 ¹⁴	Hz	
Boltzmann constant	k	1.380 658 × 10 ⁻²³	J K ⁻¹	

Solids
 Liquids
 Gases
 Artificially Prepared

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA		IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIII A
1	H Hydrogen 1.00784																	He Helium 4.002602
2	Li Lithium 6.941	Be Beryllium 9.012182											B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.0064	O Oxygen 15.9994	F Fluorine 18.9984032	Ne Neon 20.1797
3	Na Sodium 22.989770	Mg Magnesium 24.3050											Al Aluminum 26.981538	Si Silicon 28.0855	P Phosphorus 30.973761	S Sulfur 32.065	Cl Chlorine 35.453	Ar Argon 39.948
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955910	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938049	Fe Iron 55.845	Co Cobalt 58.933200	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.409	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798
5	Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90584	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.94	Tc Technetium 98	Ru Ruthenium 101.07	Rh Rhodium 102.9055	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.757	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.29

3	4	5	6	7	8	9	10	11	12
IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB
21 Sc Scandium 44.955910 [Ar]3d ¹ 4s ² 6.5615	22 Ti Titanium 47.867 [Ar]3d ² 4s ² 6.8281	23 V Vanadium 50.9415 [Ar]3d ³ 4s ² 6.7462	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s 6.7665	25 Mn Manganese 54.938049 [Ar]3d ⁵ 4s ² 7.4340	26 Fe Iron 55.845 [Ar]3d ⁶ 4s ² 7.9024	27 Co Cobalt 58.933200 [Ar]3d ⁷ 4s ² 7.8810	28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 7.6398	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s 7.7264	30 Zn Zinc 65.409 [Ar]3d ¹⁰ 4s ² 9.3942

<http://physics.nist.gov>

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

Mn: $l=2, n=5 \rightarrow S=5/2$

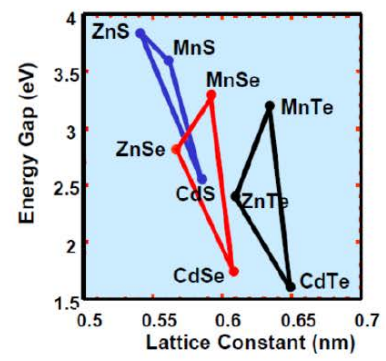
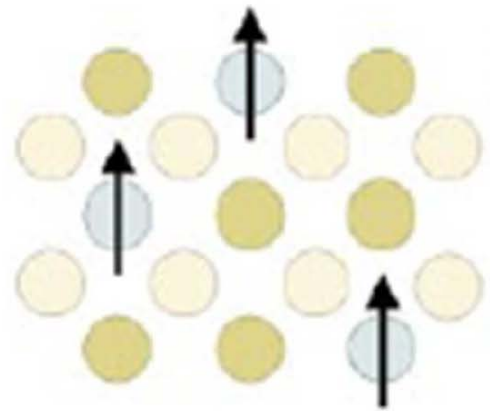
Magnetic Semiconductors

- **Early 60's: EuO and CdCr₂S₄**
 - ⇒ very hard to grow
- **Mid-80's: Diluted Magnetic Semiconductors**
 - II-VI (e.g., CdTe and ZnS) II → Mn
 - ⇒ difficult to dope
 - ⇒ direct Mn-Mn AFM exchange interaction
 - PM, AFM, or SG (spin glass) behavior
 - ⇒ present-day techniques: doping has led to FM for $T < 2\text{K}$
 - IV-VI (e.g., PbSnTe) IV → Mn
 - ⇒ hard to prepare (bulk and heterostructures), but helped understand the mechanism of carrier-mediated FM
- **Late 80's: MBE → uniform (In,Mn)As films on GaAs substrates:**
FM on p-type.
- **Late 90's: MBE → 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 T_c .

II-VI Diluted Magnetic Semiconductors

5 B Boron 10.811 $1s^2 2s^2 2p^1$ 8.2980	6 C Carbon 12.0107 $1s^2 2s^2 2p^2$ 11.2803	7 N Nitrogen 14.0064 $1s^2 2s^2 2p^3$ 14.5311	8 O Oxygen 15.9994 $1s^2 2s^2 2p^4$ 13.8181
13 Al Aluminum 26.981538 [Ne]3s ² 3p ¹ 5.9858	14 Si Silicon 28.0855 [Ne]3s ² 3p ² 8.1517	15 P Phosphorus 30.973761 [Ne]3s ² 3p ³ 10.4867	16 S Sulfur 32.065 [Ne]3s ² 3p ⁴ 10.3600
30 Zn Zinc 65.409 [Ar]3d ¹⁰ 4s ² 9.3942	31 Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p ¹ 5.9993	32 Ge Germanium 72.04 [Ar]3d ¹⁰ 4s ² 4p ² 7.8994	33 As Arsenic 74.92160 [Ar]3d ¹⁰ 4s ² 4p ³ 9.789
48 Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ² 8.9038	49 In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p ¹ 5.7864	50 Sn Tin 118.710 [Kr]4d ¹⁰ 5s ² 5p ² 7.3439	51 Sb Antimony 121.760 [Kr]4d ¹⁰ 5s ² 5p ³ 8.8084
80 Hg Mercury 200.59 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 10.4375	81 Tl Thallium 204.3833 [Hg]6p ¹ 6.1082	82 Pb Lead 207.2 [Hg]6p ² 7.4167	83 Bi Bismuth 208.98038 [Hg]6p ³ 7.2855

25 Mn Manganese 54.938049 [Ar]3d ⁵ 4s ² 7.4340
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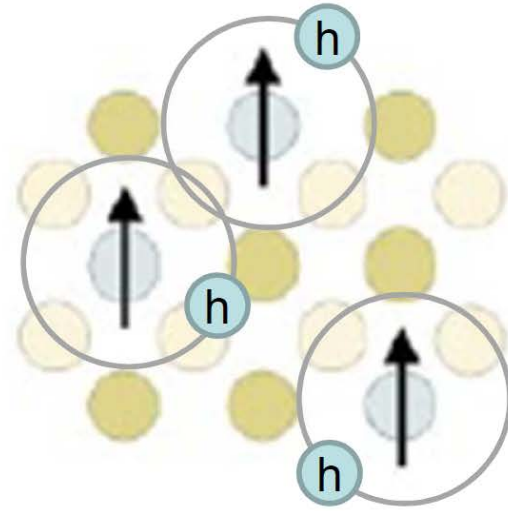
III-V Diluted Magnetic Semiconductors

5 B Boron 10.811 $1s^2 2s^2 2p^1$	6 C Carbon 12.0107 $1s^2 2s^2 2p^2$	7 N Nitrogen 14.0067 $1s^2 2s^2 2p^3$	8 O Oxygen 15.9994 $1s^2 2s^2 2p^4$
13 Al Aluminum 26.981538 $[Ne]3s^2 3p^1$	14 Si Silicon 28.0855 $[Ne]3s^2 3p^2$	15 P Phosphorus 30.973761 $[Ne]3s^2 3p^3$	16 S Sulfur 32.065 $[Ne]3s^2 3p^4$
30 Zn Zinc 65.409 $[Ar]3d^{10} 4s^2$	31 Ga Gallium 69.723 $[Ar]3d^{10} 4s^2 4p^1$	32 Ge Germanium 72.64 $[Ar]3d^{10} 4s^2 4p^2$	33 As Arsenic 74.92160 $[Ar]3d^{10} 4s^2 4p^3$
48 Cd Cadmium 112.41 $[Kr]4d^{10} 5s^2$	49 In Indium 114.818 $[Kr]4d^{10} 5s^2 5p^1$	50 Sn Tin 118.71 $[Kr]4d^{10} 5s^2 5p^2$	51 Sb Antimony 121.760 $[Kr]4d^{10} 5s^2 5p^3$
80 Hg Mercury 200.59 $[Xe]4f^{14} 5d^{10} 6s^2$	81 Tl Thallium 204.3833 $[Hg]6p^1$	82 Pb Lead 207.2 $[Hg]6p^2$	83 Bi Bismuth 208.98038 $[Hg]6p^3$
			84 Po Polonium (209) 8.414 $[Hg]6p^4$

+

25 Mn Manganese 54.938049 $[Ar]3d^5 4s^2$
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=

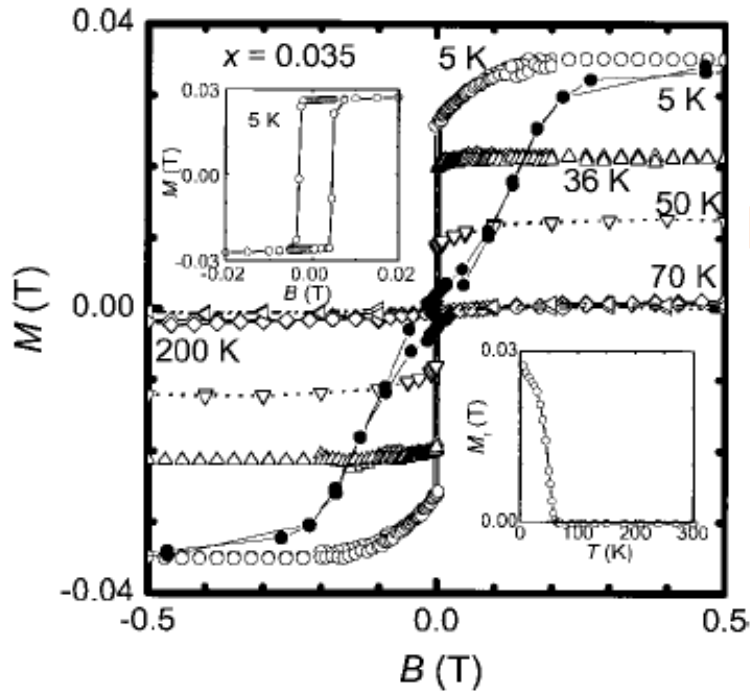


not to scale

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

Mn-doped GaAs

$x = 0.035$

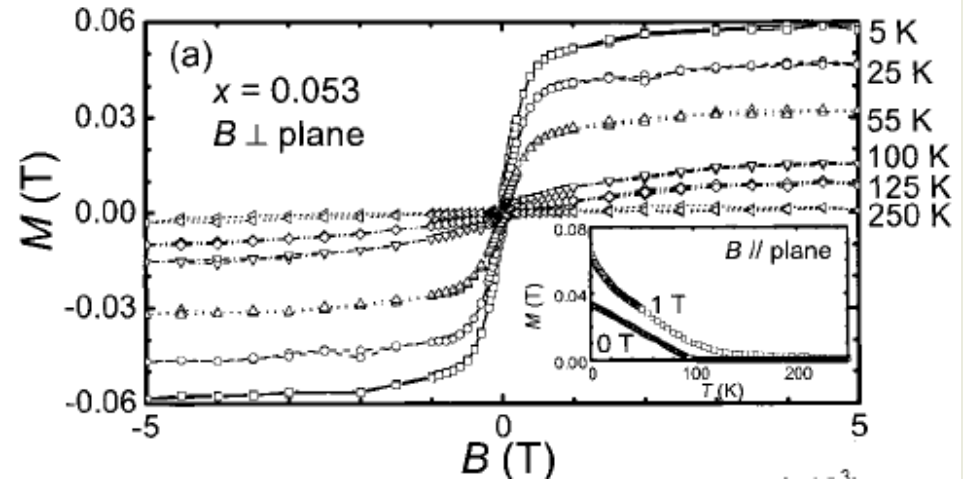
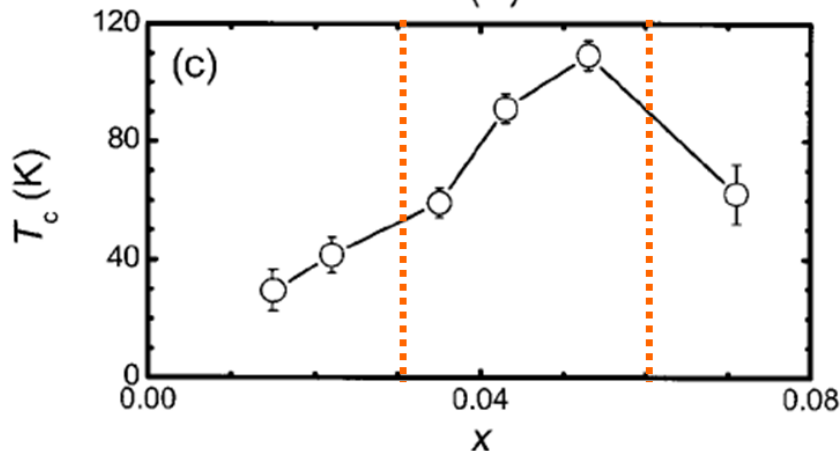


- Open symbols: B in-plane
- hysteresis \Rightarrow FM with easy axis in plane;
- remanence vs. $T \Rightarrow T_c \sim 60$ K

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

$x = 0.053$

$T_c \sim 110$ K



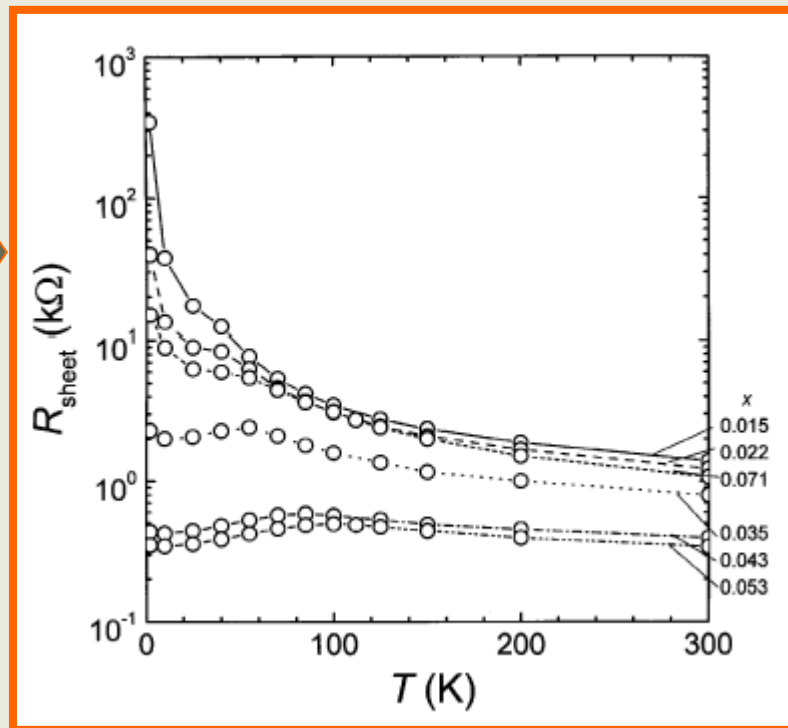
Mn-doped GaAs

Resistance measurements on samples with different Mn concentrations:

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

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

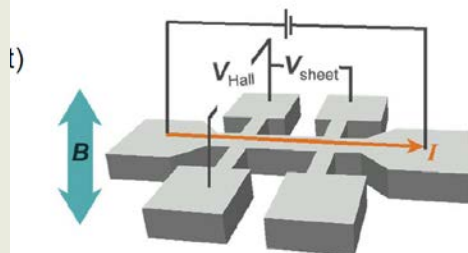
\Rightarrow Reentrant MIT



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

Transport of (Ga,Mn)As

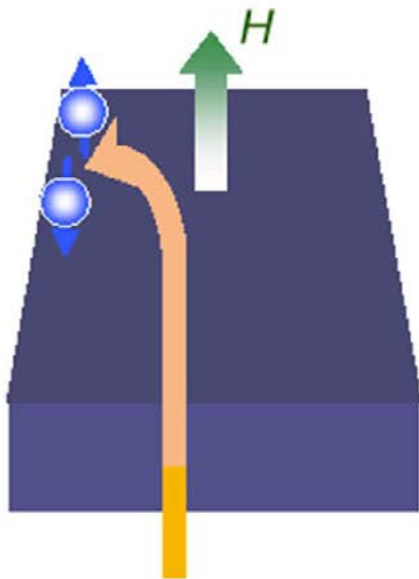
$$R_{\text{Hall}} = (R_0/d)B + (R_S/d)M_{\perp}$$



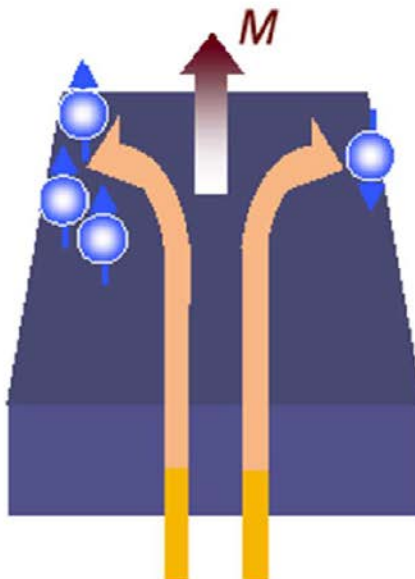
$$R_{\text{Hall}} = V_{\text{Hall}}/I$$
$$R_{\text{sheet}} \propto V_{\text{sheet}}/I$$

Hall Effects

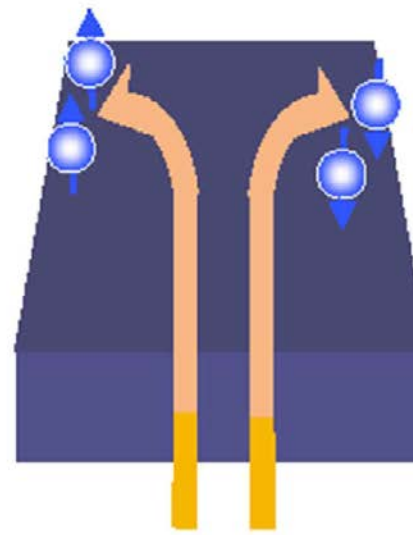
Ordinary Hall effect



Anomalous Hall effect

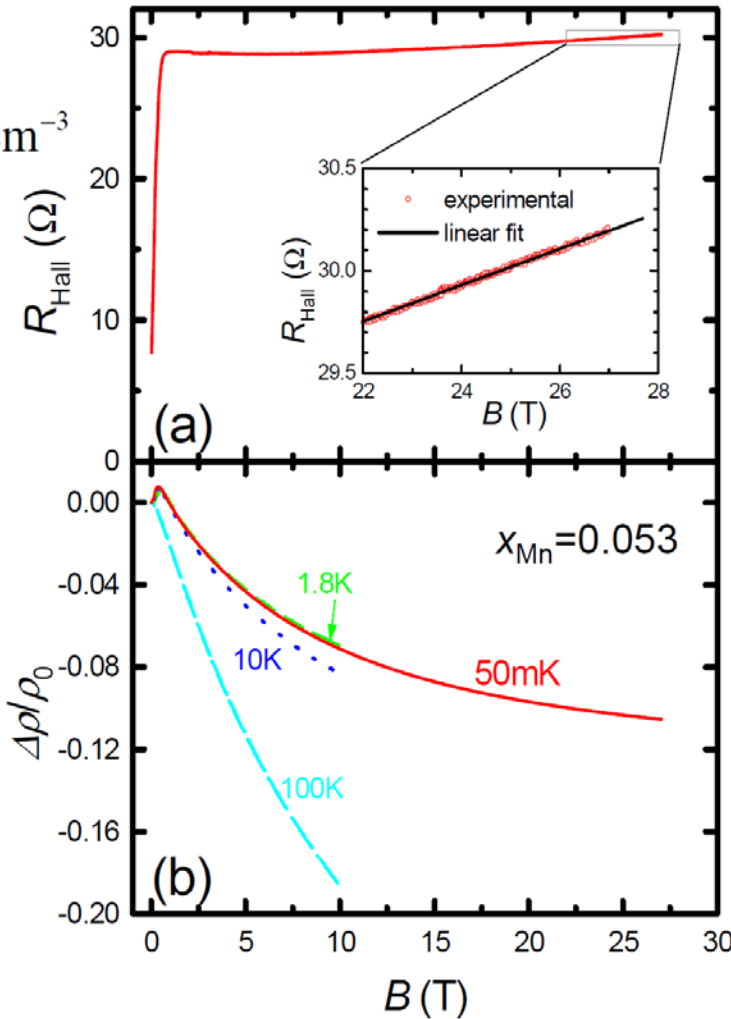


Spin Hall effect



Ga_{0.947}Mn_{0.053}As

[Mn] = 1.2 × 10²¹ cm⁻³



$\rho = 3.5 \times 10^{20} \text{ cm}^{-3}$
(30% of Mn)

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

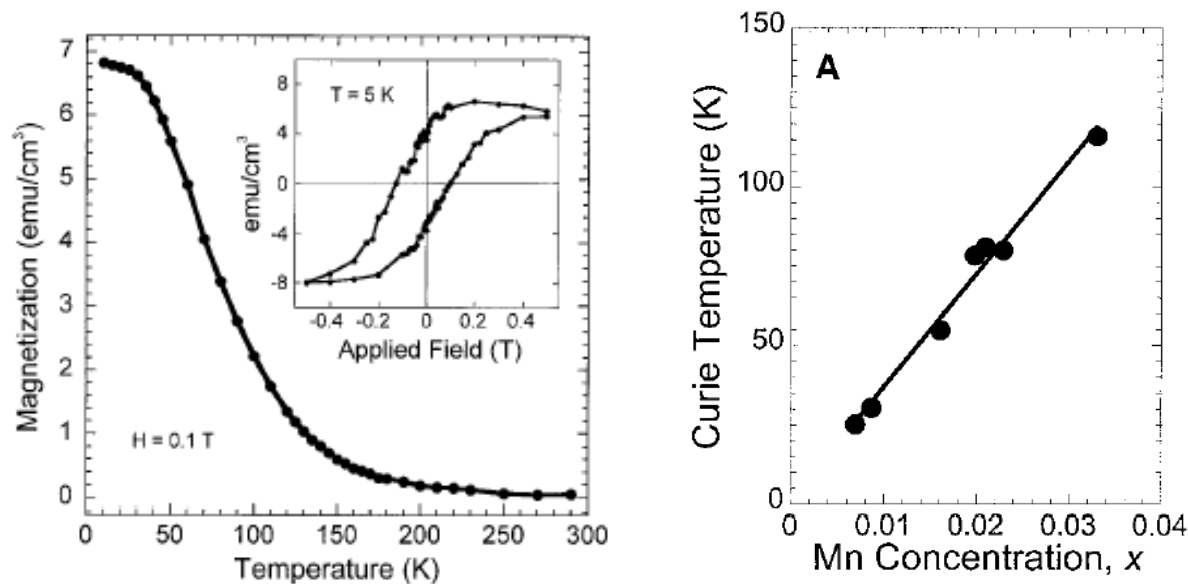
Silicon-Compatible DMS

A Group-IV Ferromagnetic Semiconductor: $\text{Mn}_x\text{Ge}_{1-x}$

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||

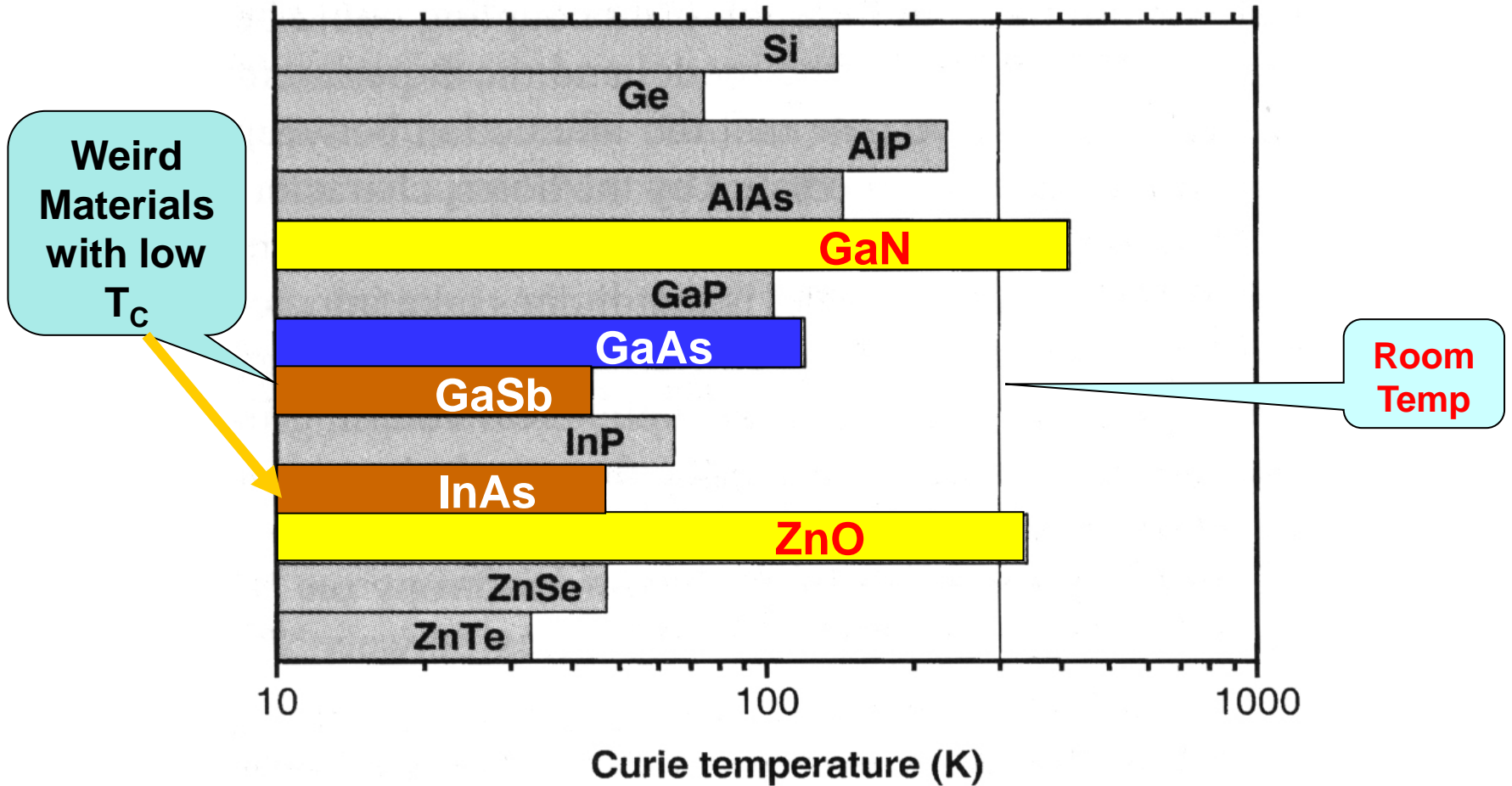
Naval Research Laboratory, Washington, DC

SCIENCE VOL 295 25 JANUARY 2002



$T_C \sim 116\text{K} \ll \text{RT}$

Predicted Curie Temperatures



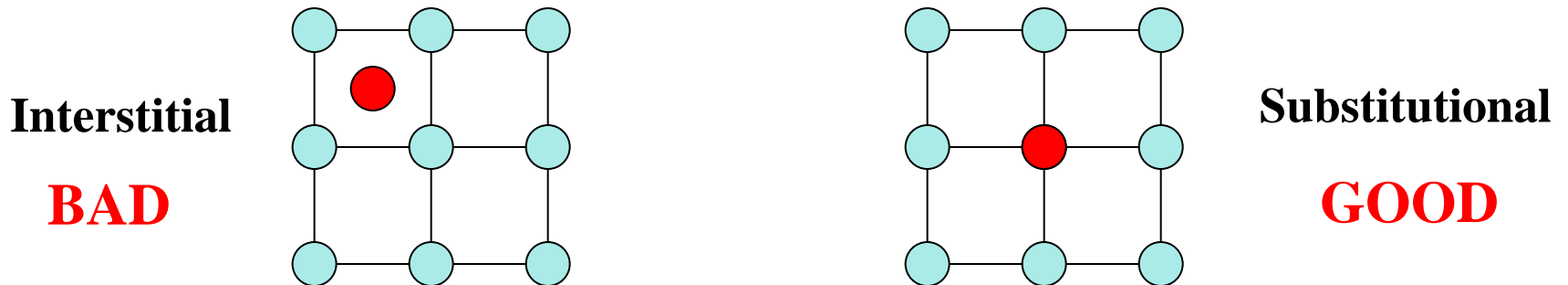
Primary Challenge: Increase T_C to Room Temperature or Higher

Generic guides:

- “...any strategy that increases the hole density near Mn ions will increase T_C ...”

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

- “...more substitutional, less interstitials...”



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. Weiering, 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. Weiering, 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

Outline

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

Subsurfactant Epitaxy: Collaborators

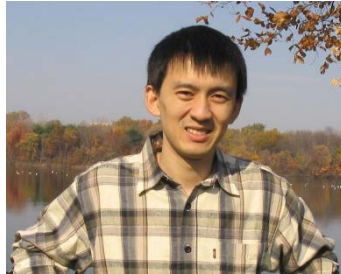
Theory

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



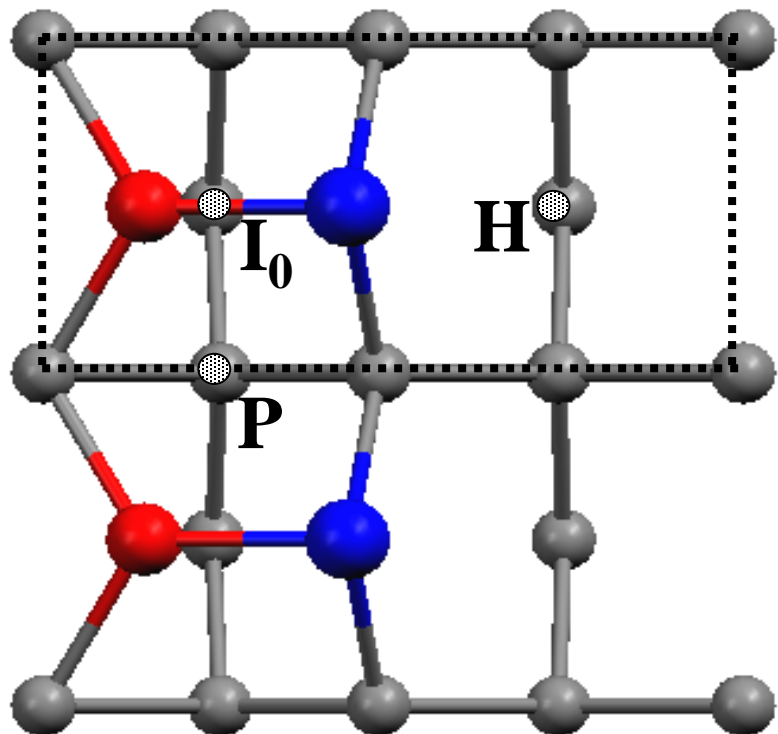
Dr. Klaus van Benthem

Dr. Matthew Chrisholm

ORNL

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

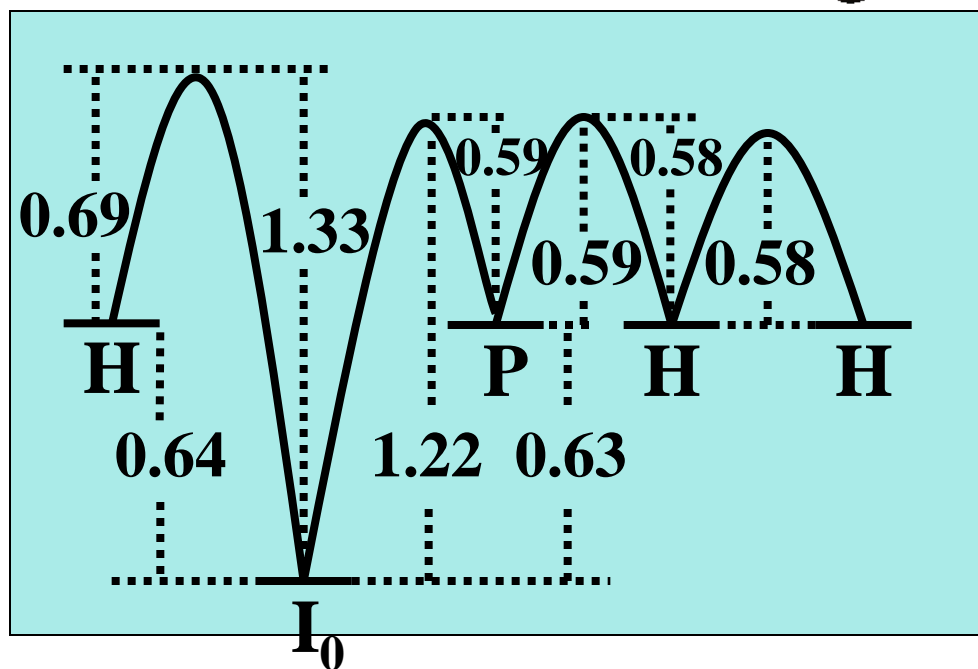
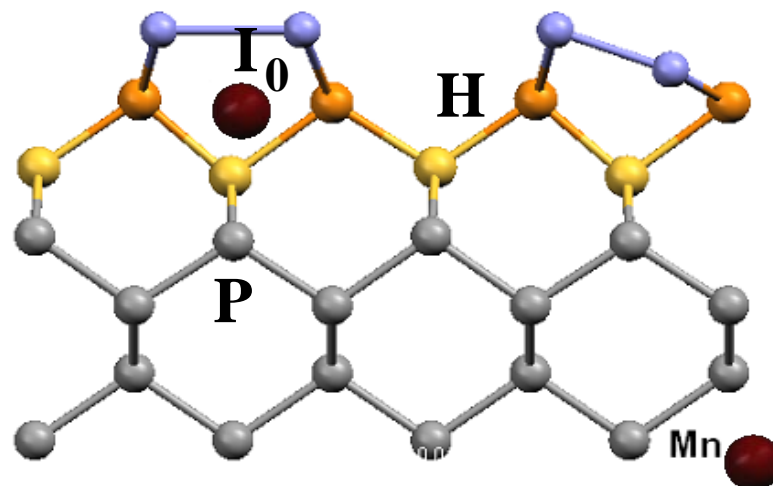
Top View



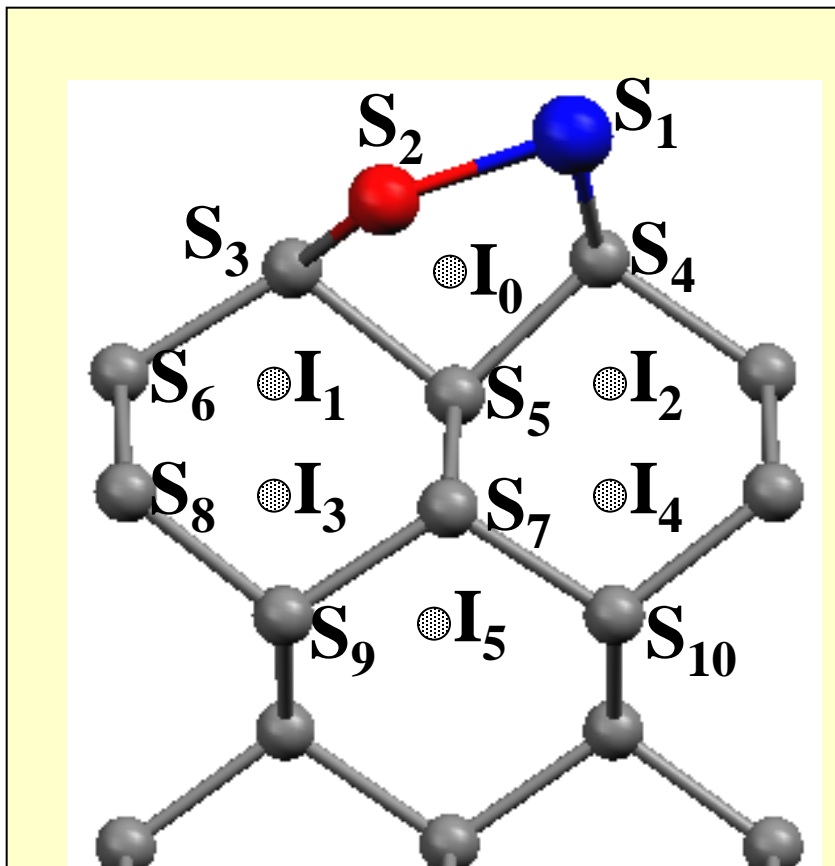
● Ge up-atom ● deeper layer
● Ge down-atom

- DFT-GGA calculations
- spin polarized

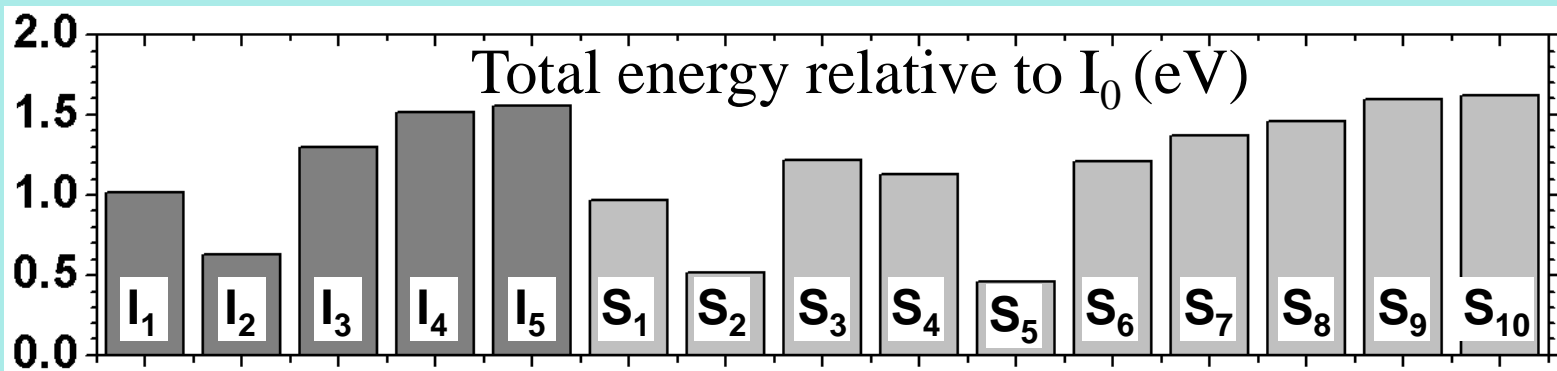
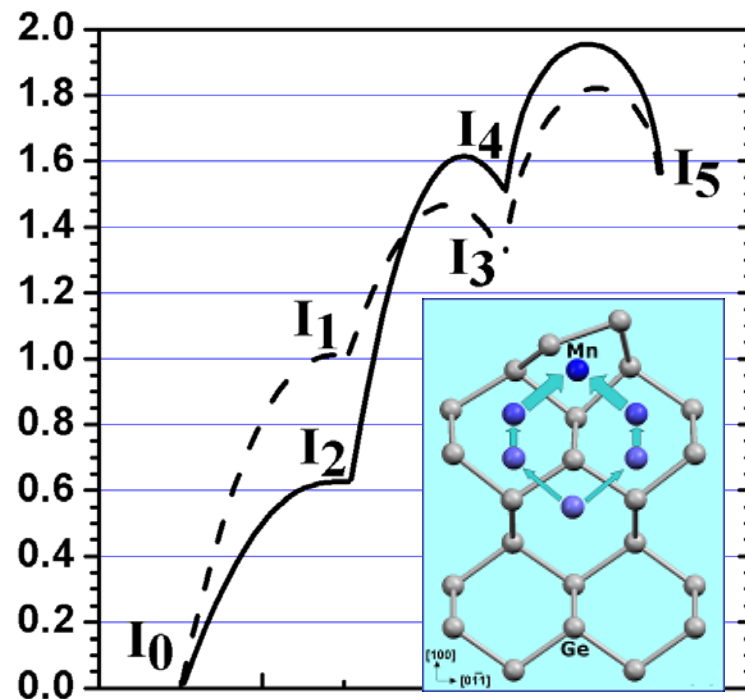
Side View



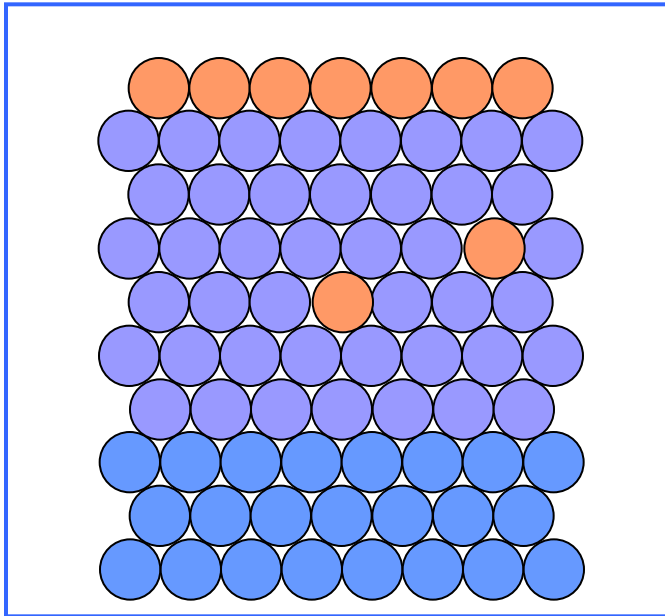
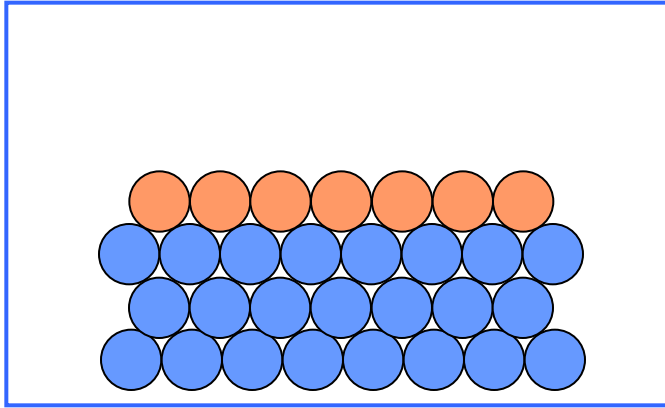
Subsurface segregation of Mn on Ge(100)-2x1



“Subsurfactant Action”

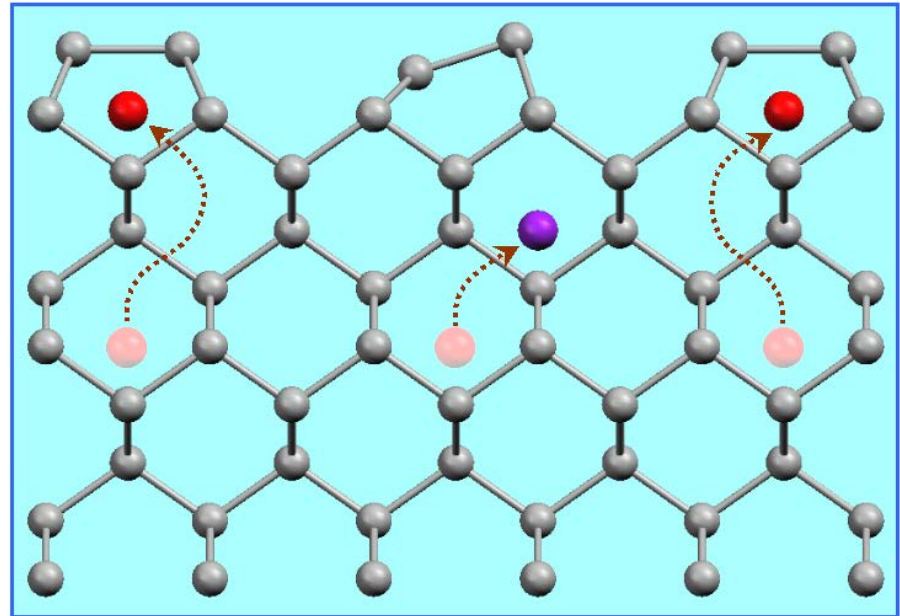
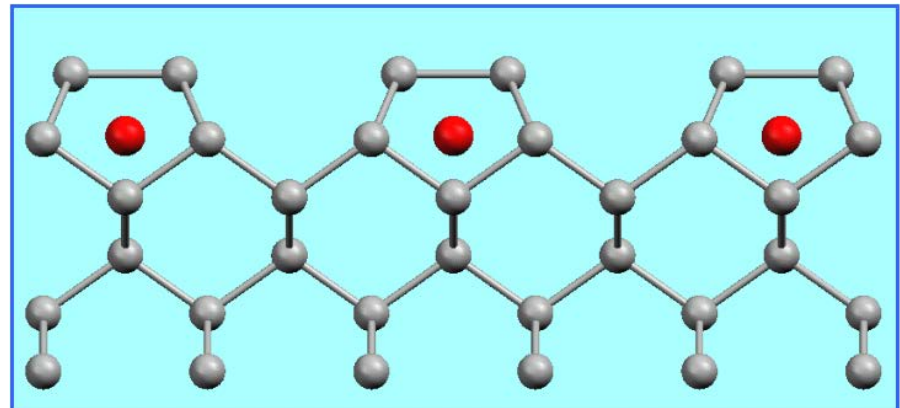


Surfactants vs. Subsurfactants



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

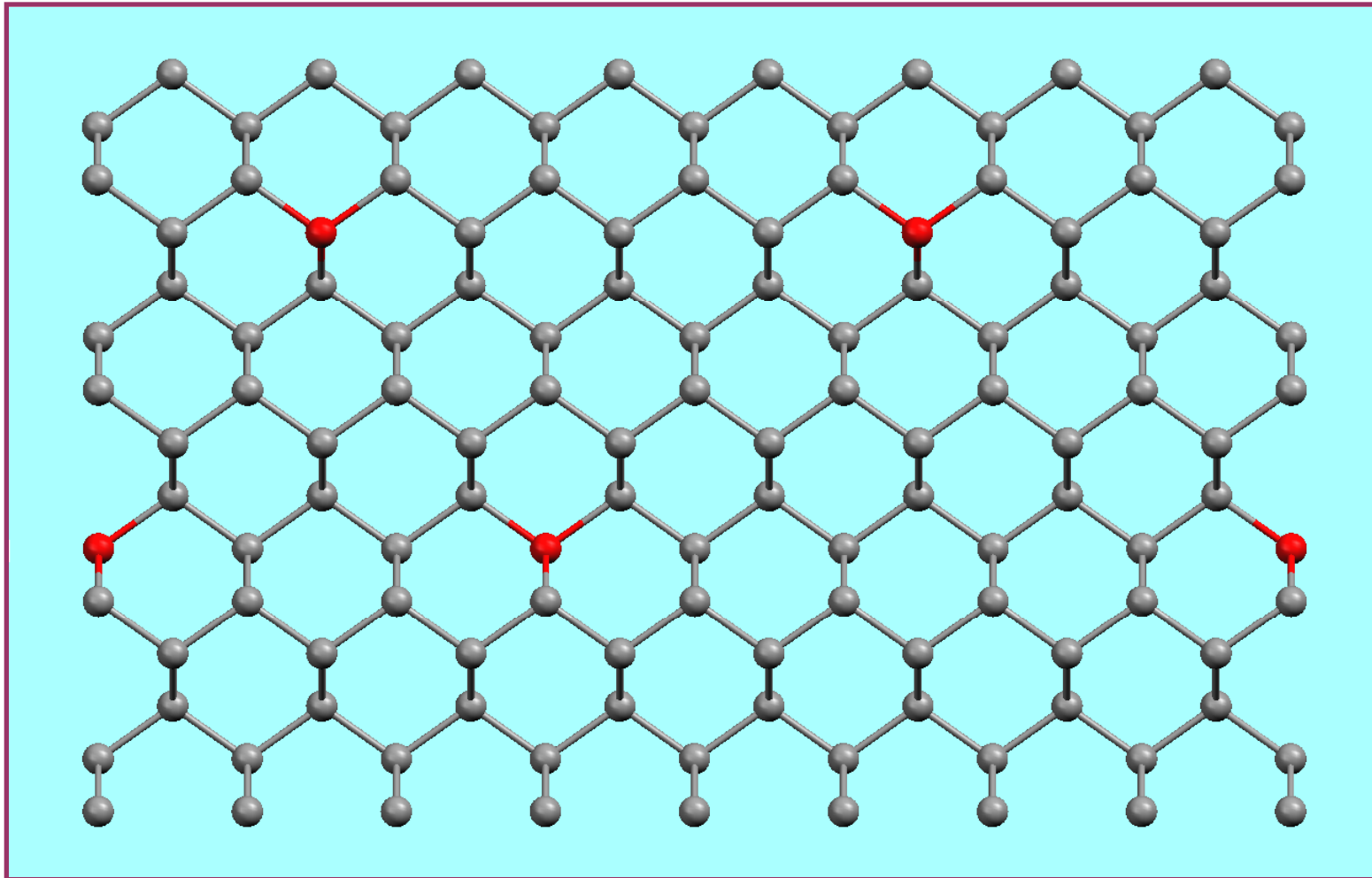
Trapping: bad



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

Trapping: good!!!

Doping via Subsurface Epitaxy?



Ge

Ge: Mn

Ge

Ge: Mn

Ge

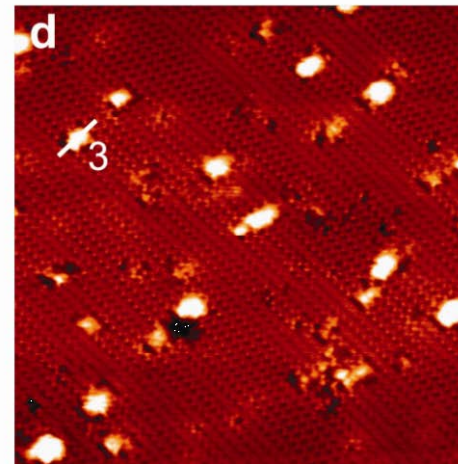
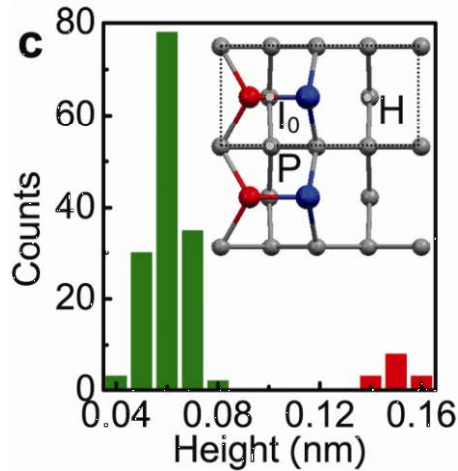
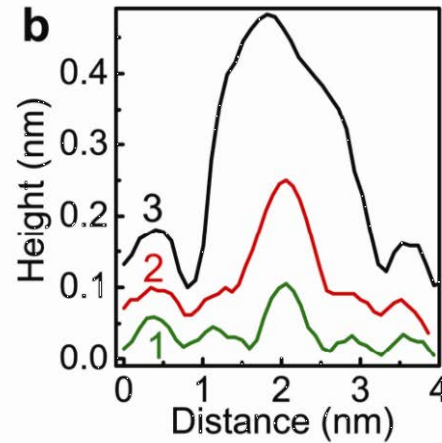
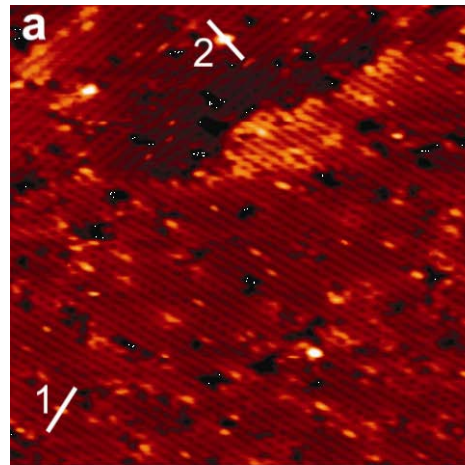
Notable Results on the Theory Side

- 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 destabilizes 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

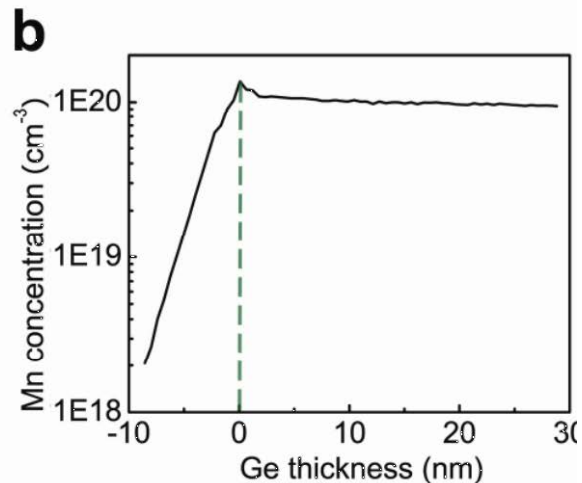
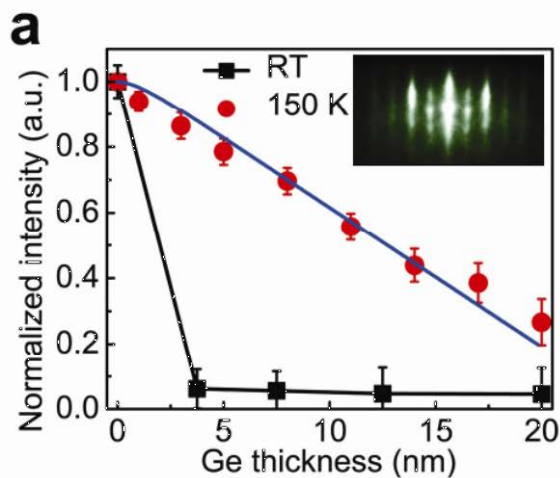
Low T:
Scattered



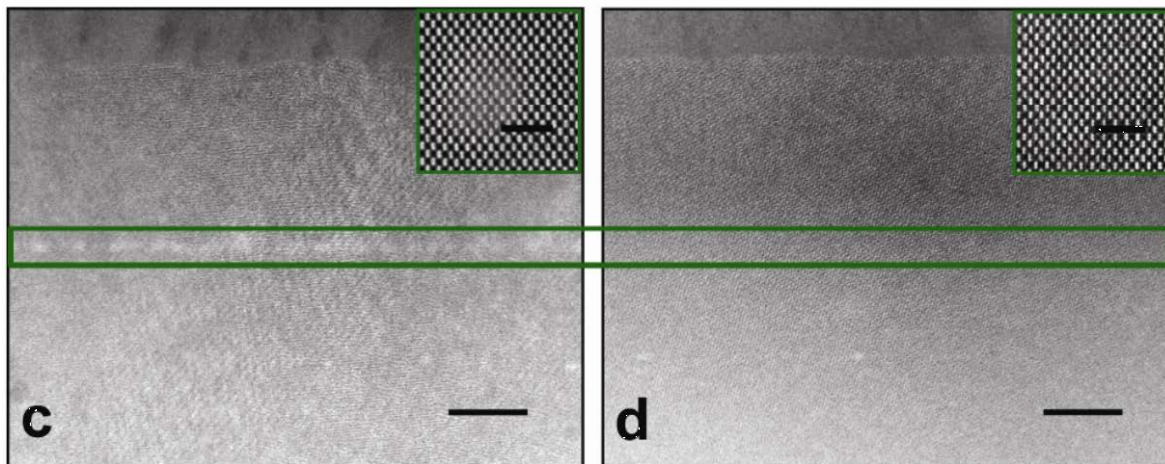
RT:
Clustered

Experimental Confirmation: Floating and doping

XPS

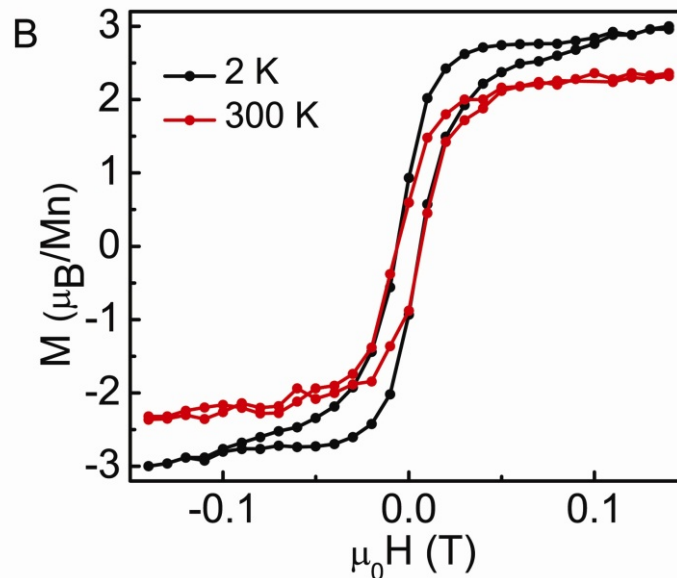
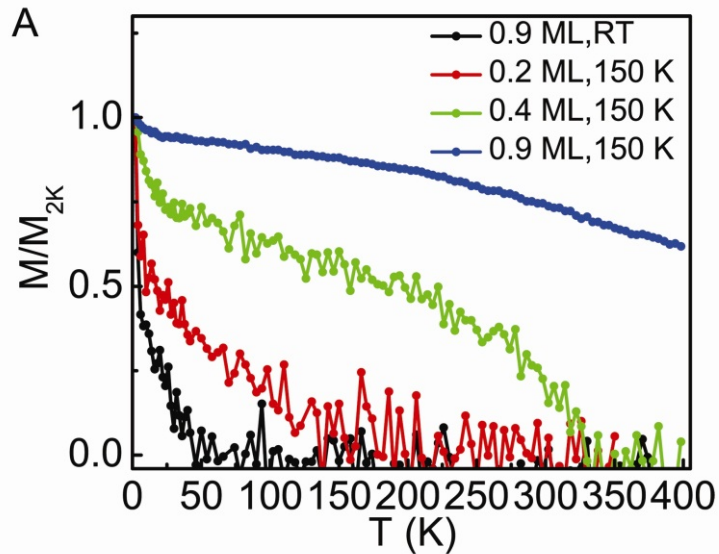


SIMS



X-STEM

Key Discovery **beyond** Theoretical Expectation:

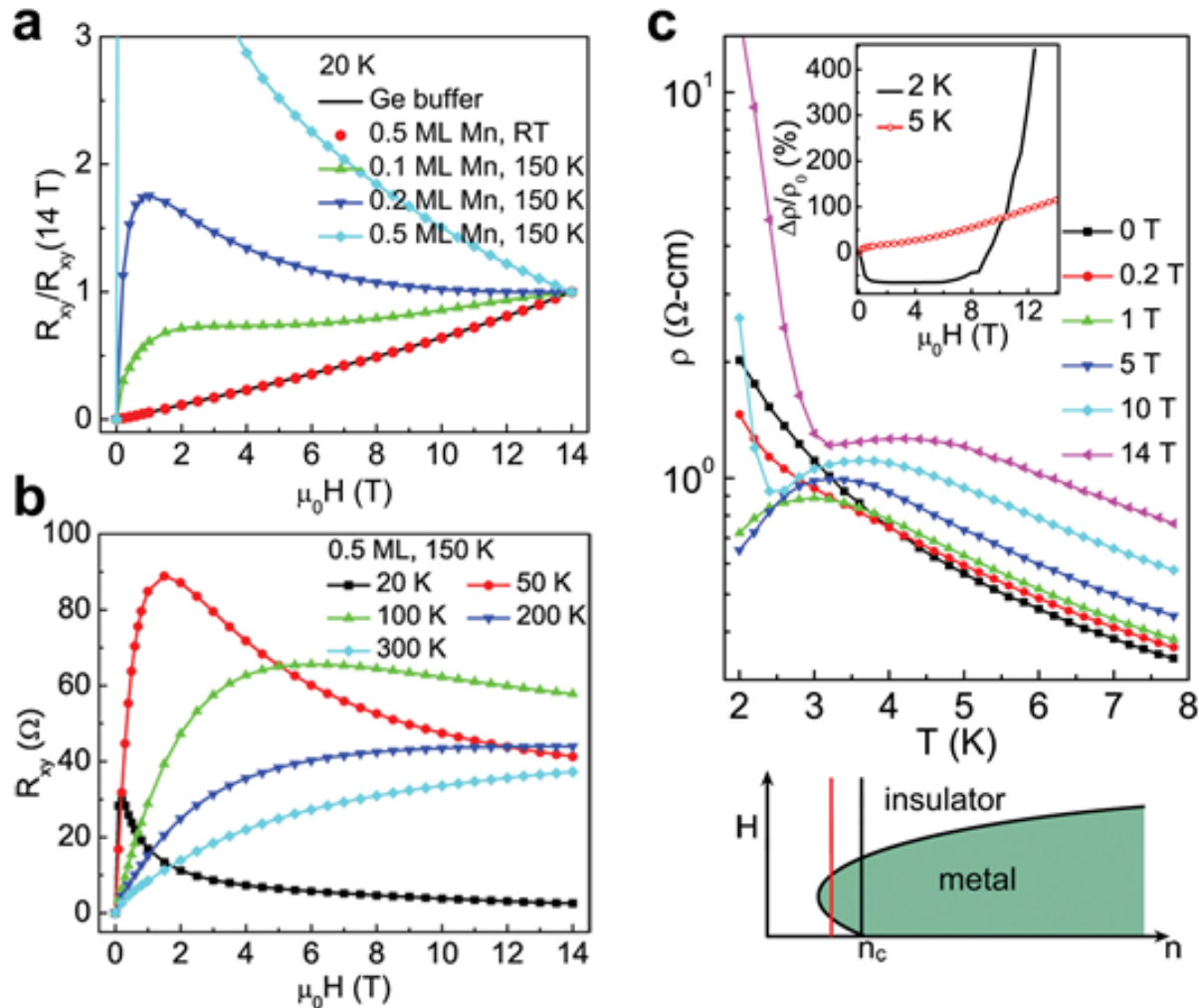


**A sweet treat from
Mother Nature:**

**$T_c > 400\text{K}$
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 contaminants 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

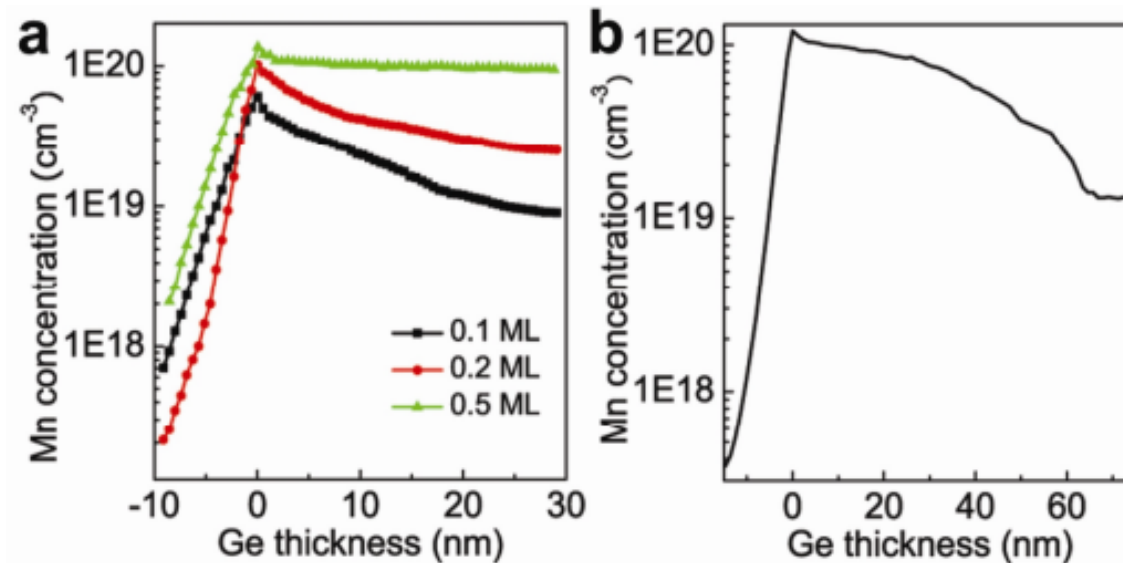
- A novel growth mode, **Subsurfactant Epitaxy**, has been proposed theoretically and confirmed experimentally.
- Most surprisingly, it offered an optimal way to dope the right amount of Mn into (presumably) the right sites inside Ge, resulting in a striking increase of $T_c > 400\text{K}$ at the nominal dopant levels of $\sim 0.23\%$!
- **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 ($T_c > 400\text{K}$) ?

Outline

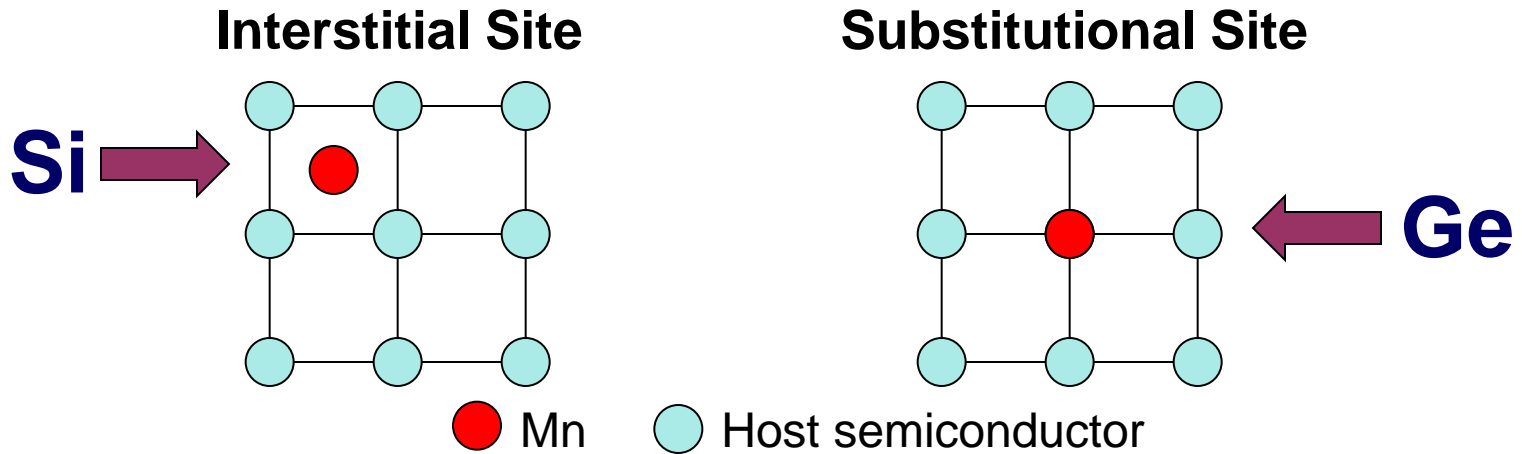
- Introduction to Spintronics
- Introduction to DMS
- Subsurface Epitaxy of DMS Materials
- **Non-Compensated n-p Codoping of DMS Materials**

B. Aided by Conventional Electronic Dopants

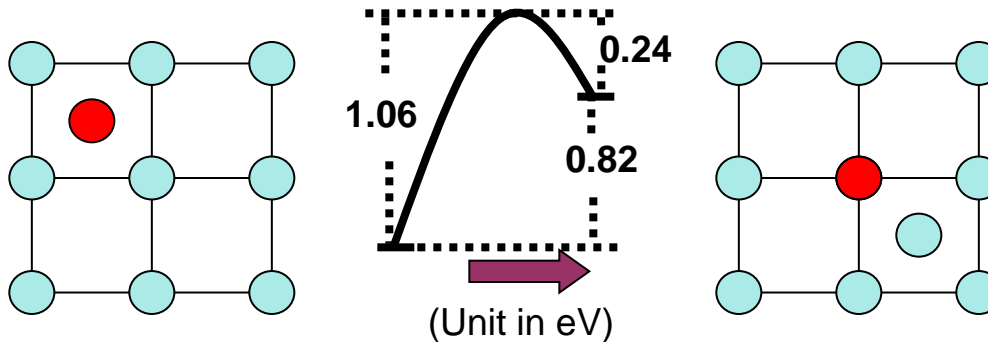
Prediction: Wenguang Zhu, ZZ, E. Kaxiras, PRL (2008)

Also: from DMS to DMO

Preference of Mn in Bulk Si and Ge

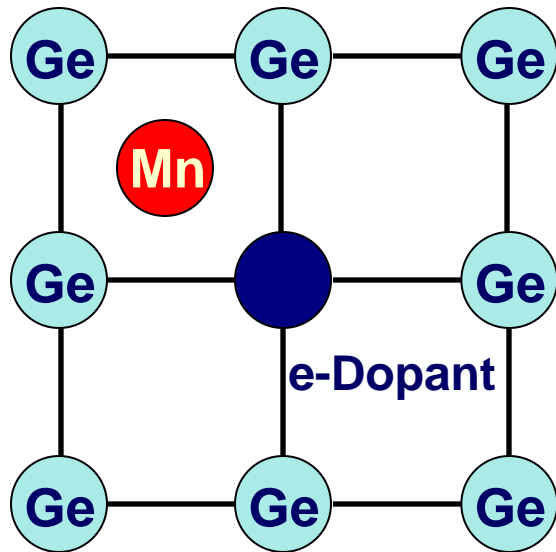


- In bulk Si, Mn prefers interstitial sites by 0.58 eV.
- In bulk Ge, Mn prefers substitutional sites by 0.63 eV, but has to overcome an energy barrier of **1.06 eV** to replace a host Ge atom.



Conjecture: Can An e-Dopant Help?

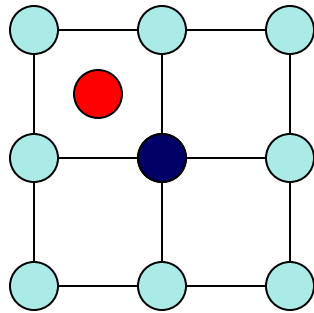
The assistance of n-type or p-type dopants in the bulk structures might make it easier for the Mn atoms to be incorporated into substitutional sites.



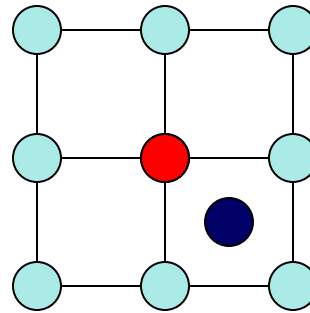
p		n	
aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	

Direct Place Exchange?

(a) Initial State



(b) Final State

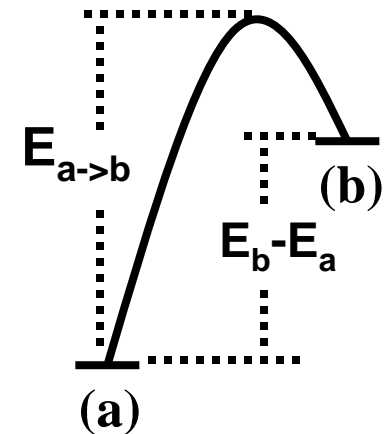


- Mn
- Semiconductor
- Dopant

Si		Ge		
Dopant	$E_b - E_a$	Dopant	$E_b - E_a$	$\epsilon_{a \rightarrow b}$
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	

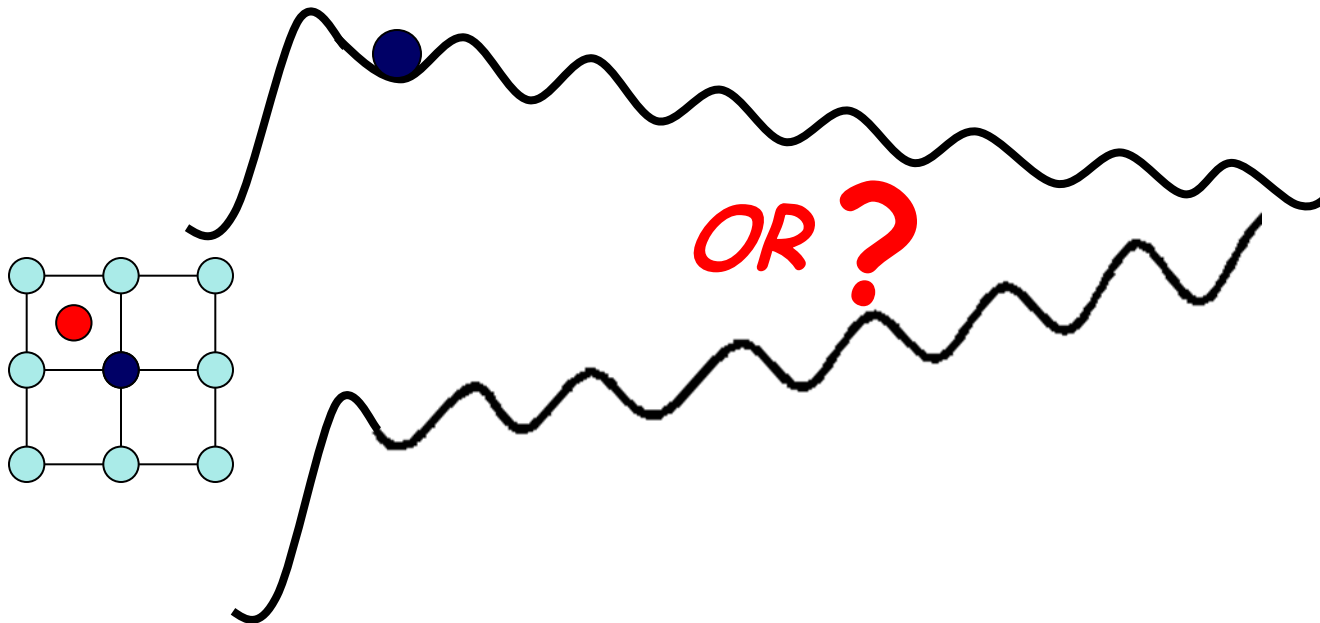
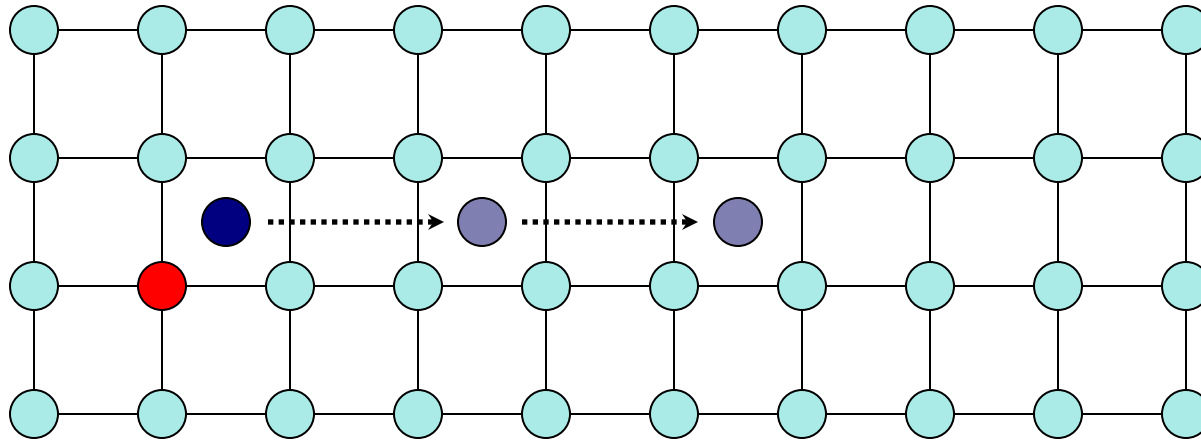
(Unit in eV)

Energy Profile

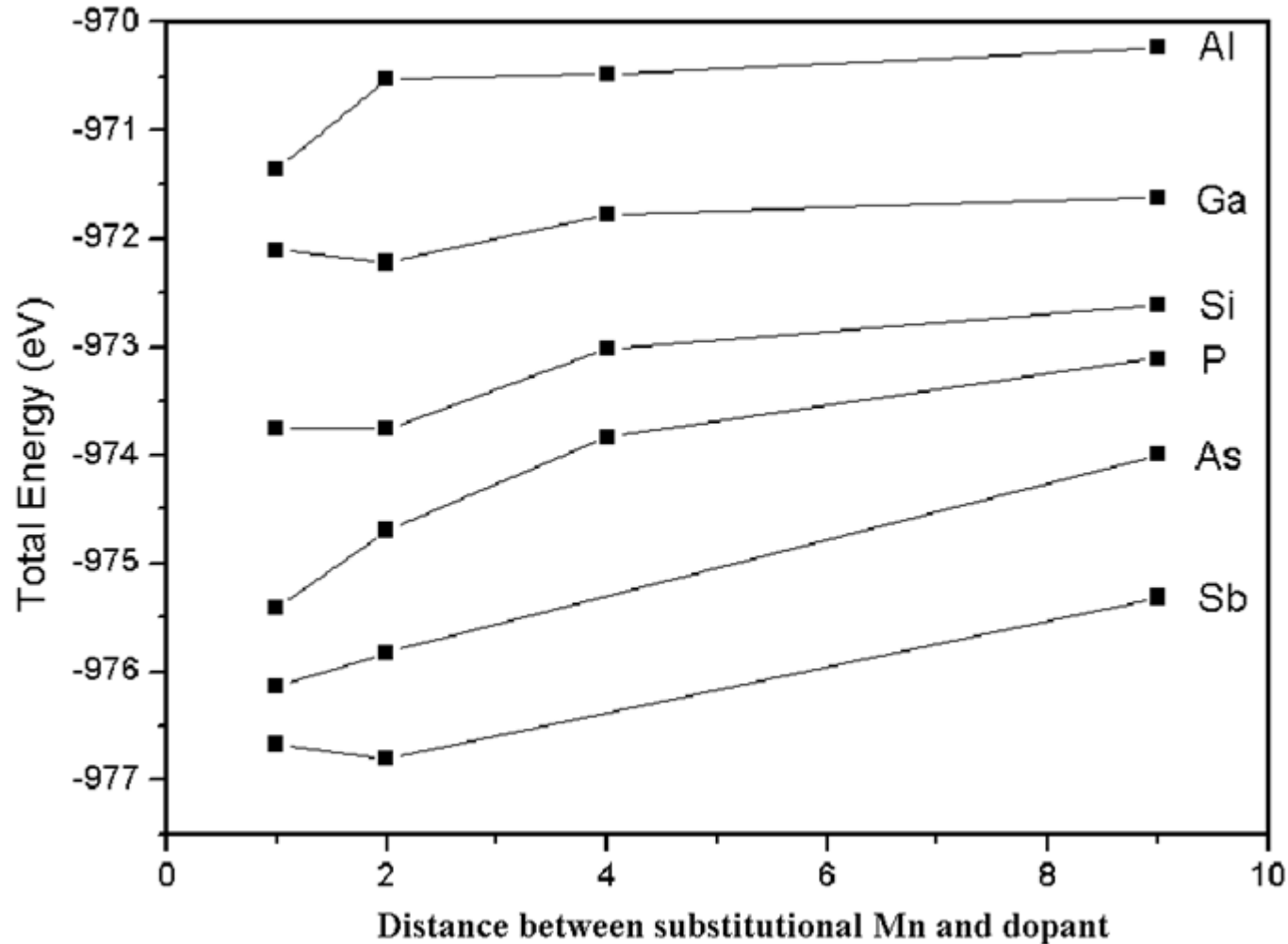


Is the Final State Stable or not ?

● Mn ● Semiconductor ● Dopant



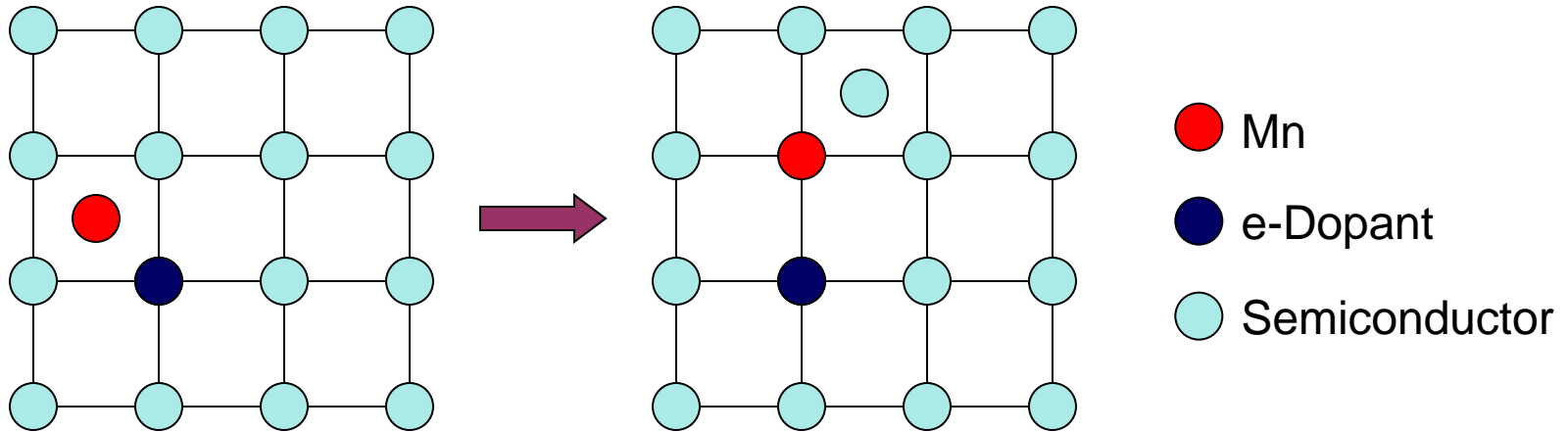
Dopant Can Not Easily Diffuse Away



First try fails !

Mn Substitutional Dopping Aided by n

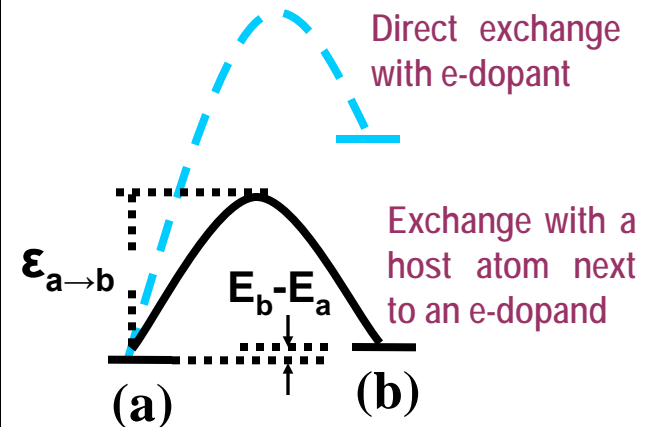
An e-dopant still occupies a substitutional site, while a neighboring interstitial Mn atom exchanges with a host semiconducting atom.



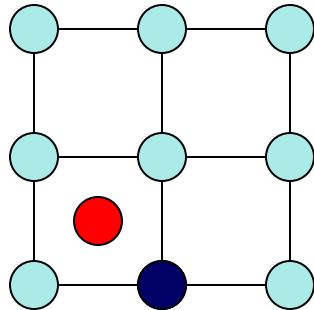
Si		Ge		
Dopant	$E_b - E_a$	Dopant	$E_b - E_a$	$\epsilon_{a \rightarrow b}$
Si	2.03	Ge	0.82	
P	0.89	P	0.03	0.34
As	1.09	As	0.05	0.25
Sb	1.27	Sb	0.22	0.38
Al	2.05	Al	1.54	
Ga	2.43	Ga	1.52	

(Unit in eV)

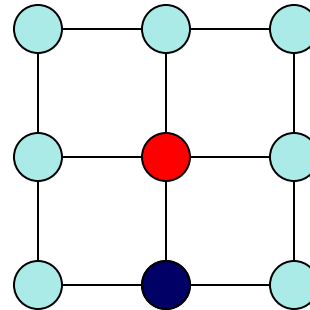
Energy Profile



Formation Energy of a Mn/e-dopant Substitutional Pair



(a)



(b)

	Relative formation energy: $(E_b + \mu_{\text{host}}) - E_a$			
	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)

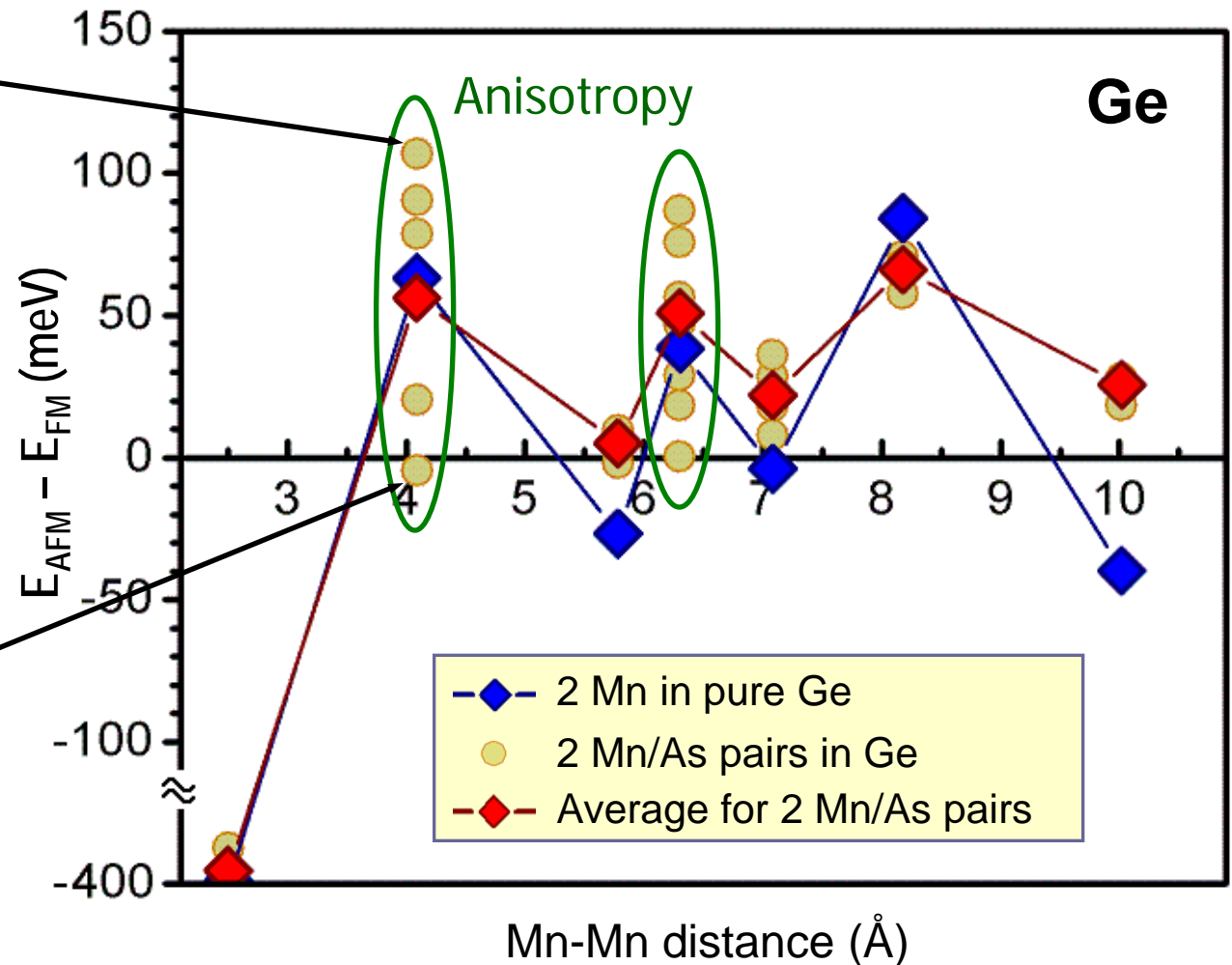
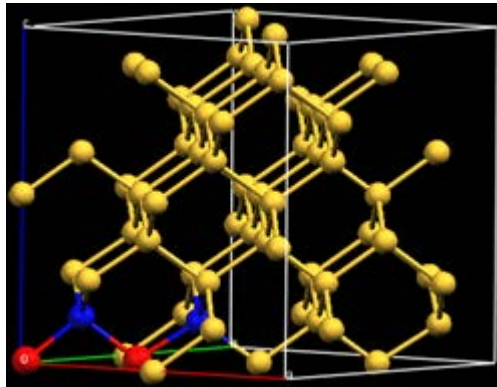
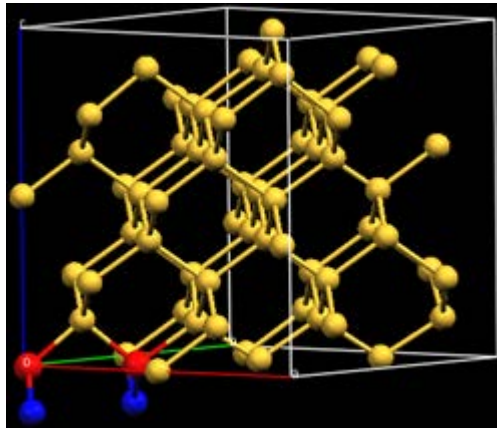
p-type Substitutional Mn



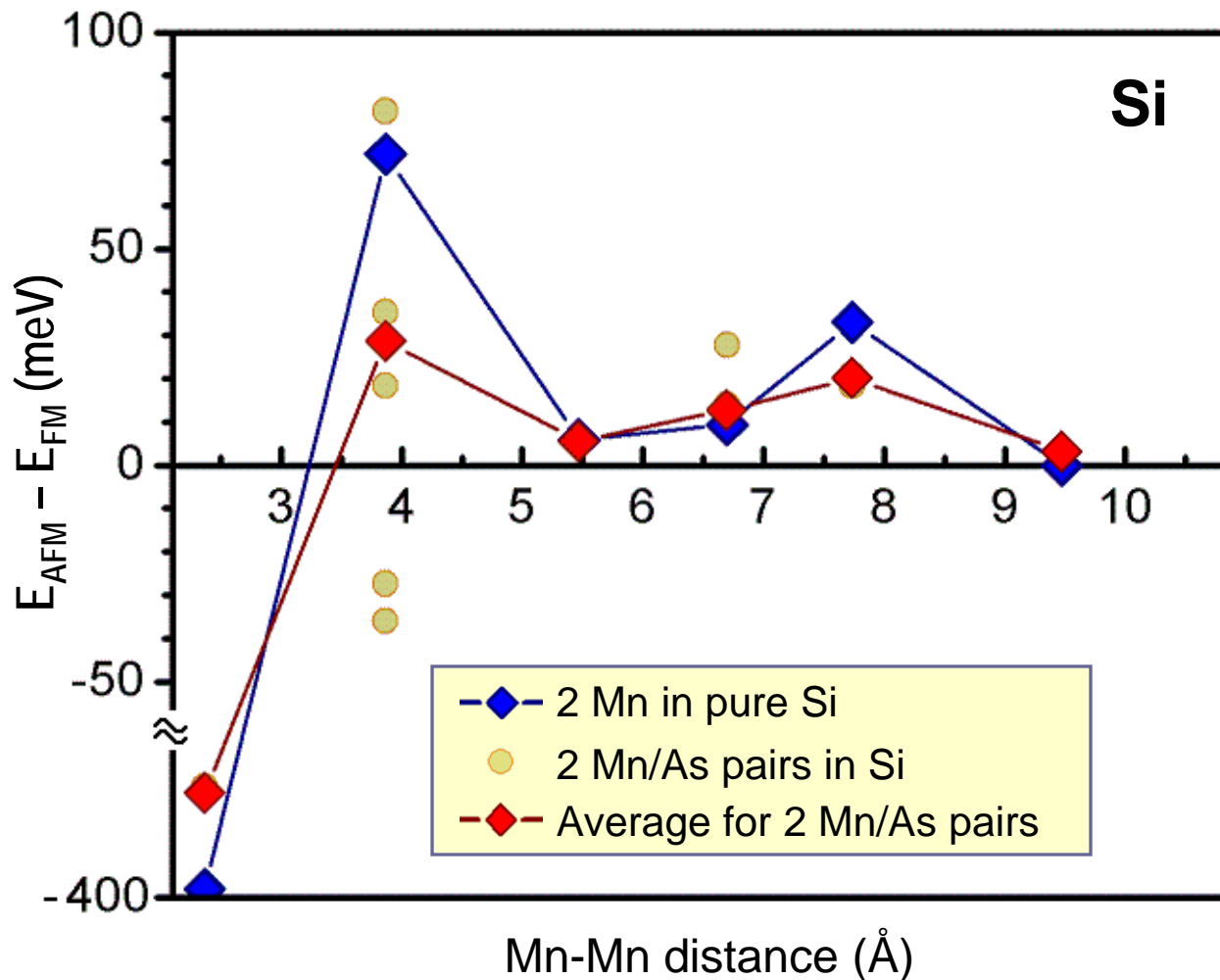
Coulomb attraction

n-type e-dopant

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?

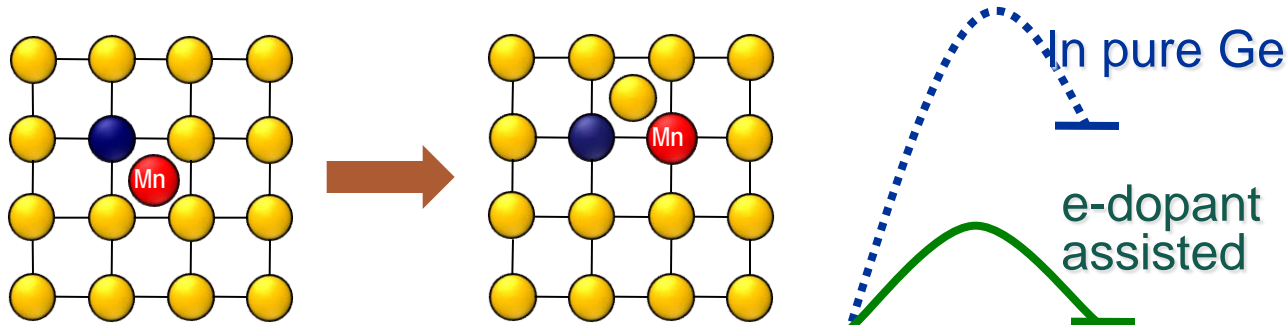
- From structures to transport?

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 coupling 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



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

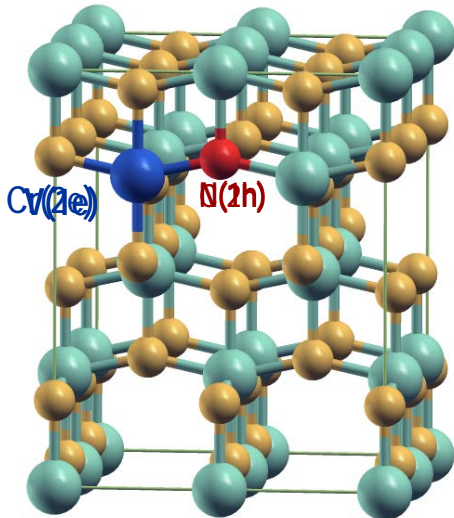
See also:
Mn in III-V as DMS
Dietl et al.
Nature Materials 2007.

Substitutional Mn
(+2 or +3)

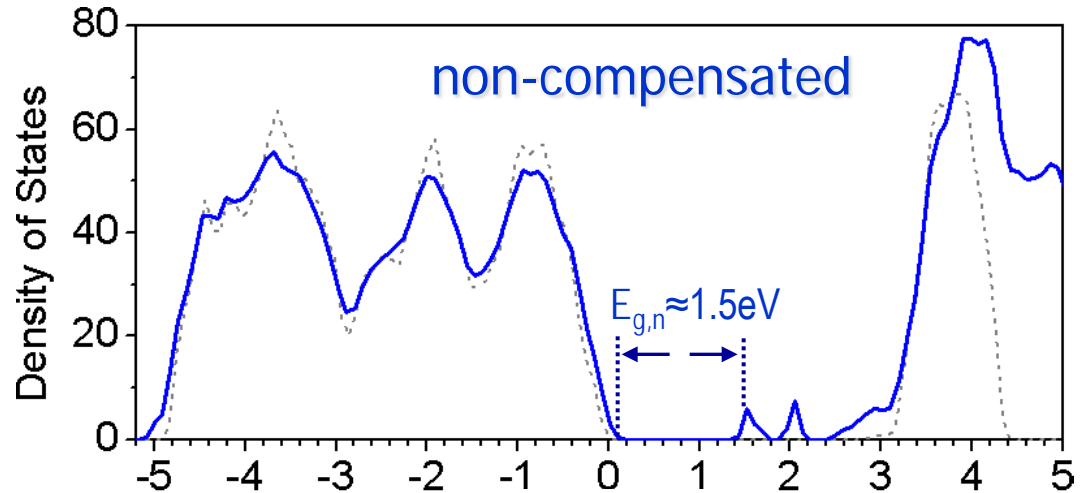
n -type e-dopant
(-1)

Coulomb attraction

Anatase TiO_2




scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998
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Looking Forward

- Will the favoring of FM order and the enhanced magnetic anisotropy translate into higher T_c ?
- 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

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

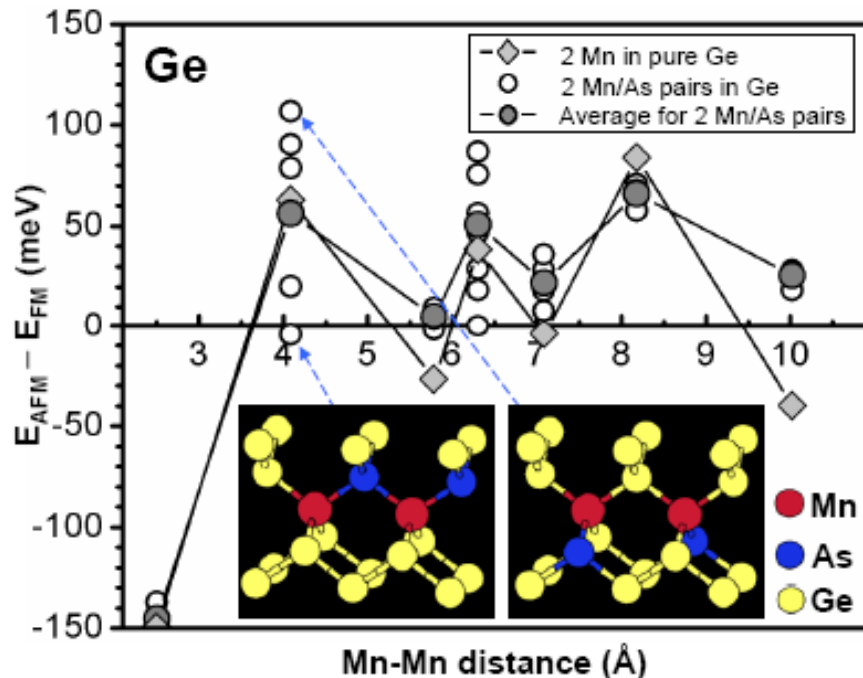




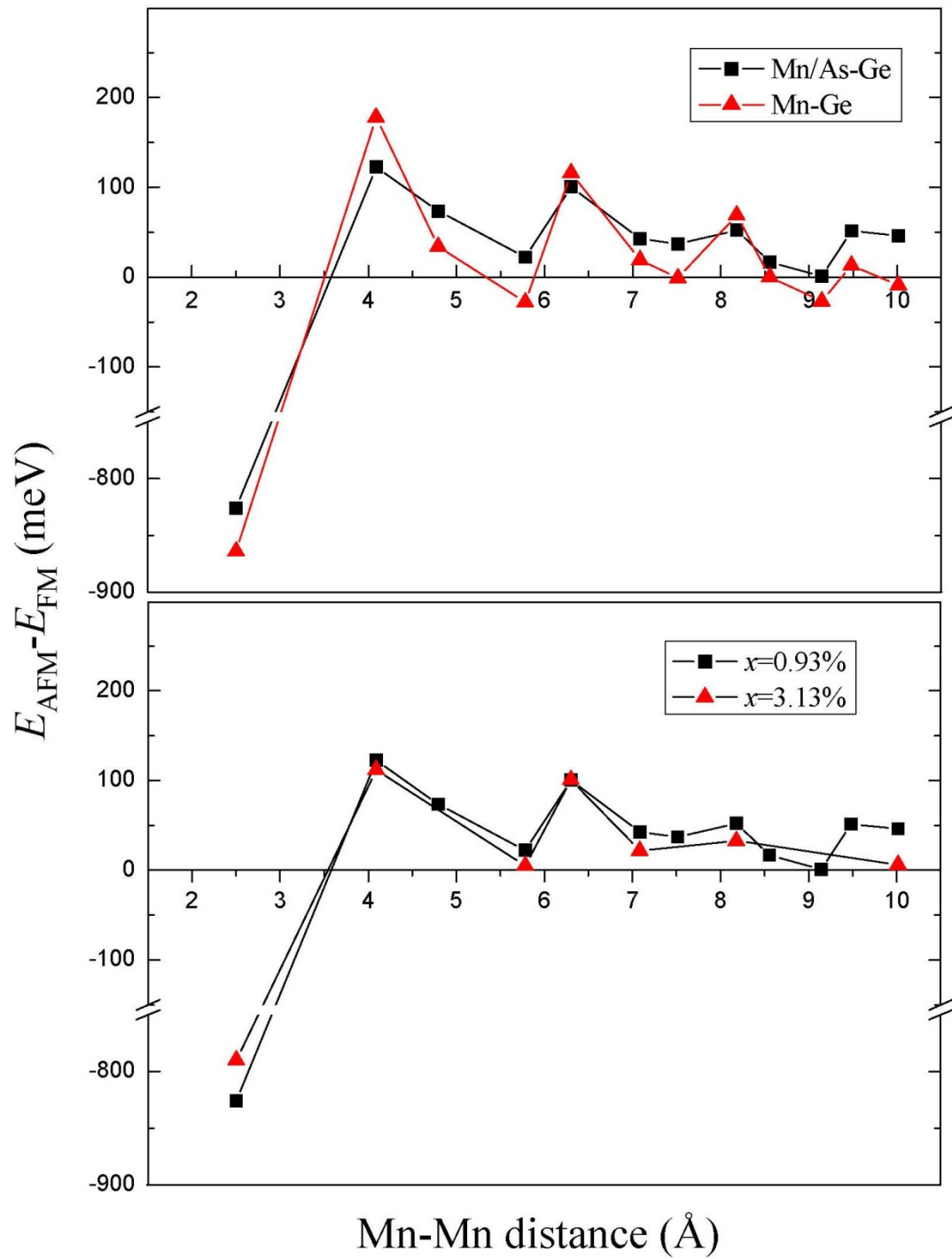
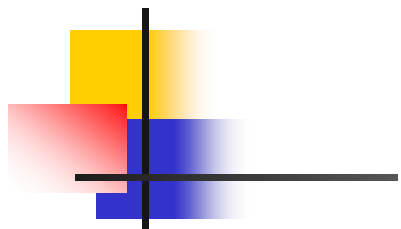
Curie temperature: A Two-Step Approach

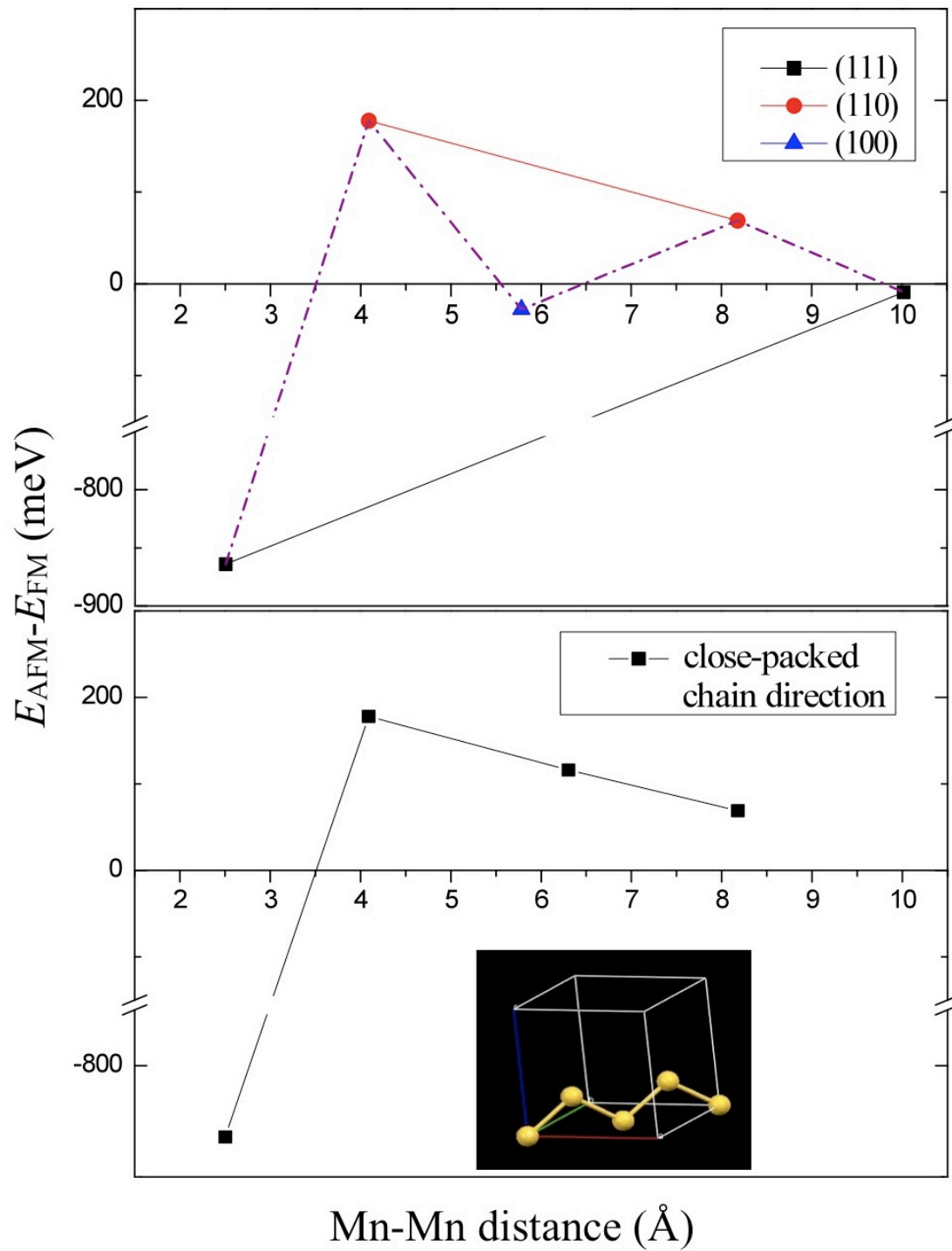
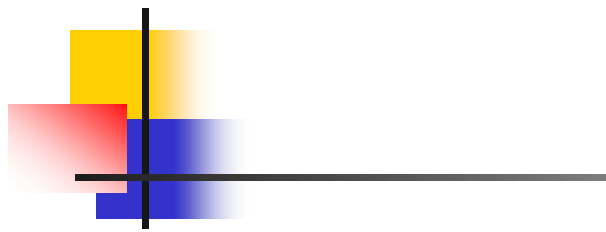
- 1. Exchange interaction constants are determined from supercell *ab initio* calculations.
- 2. Curie temperature is determined by Monte Carlo simulation, using the interaction parameters calculated in 1.
-
-

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)







Curie temperature

- Metropolis algorithm
- 4th-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 $\Delta E < 0$, flip the spin, otherwise do the flipping with a probability:

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

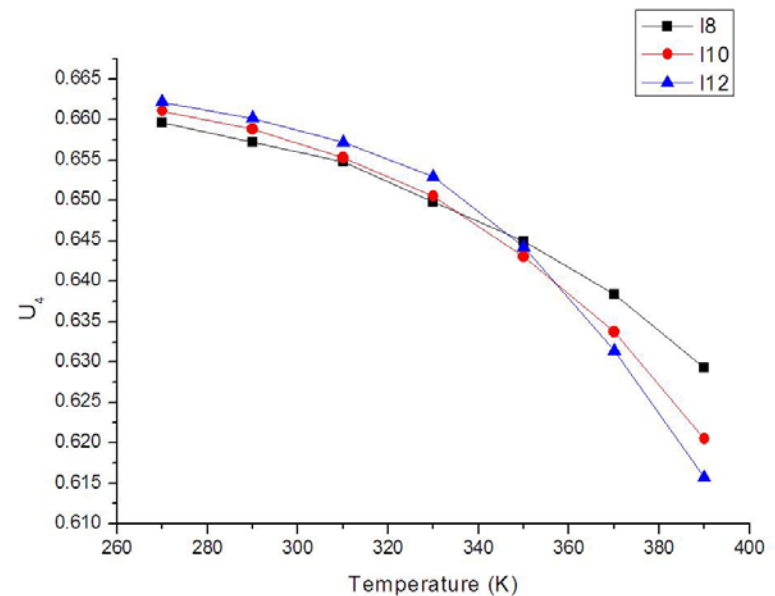
- Go to step 1

Curie temperature (contd.)

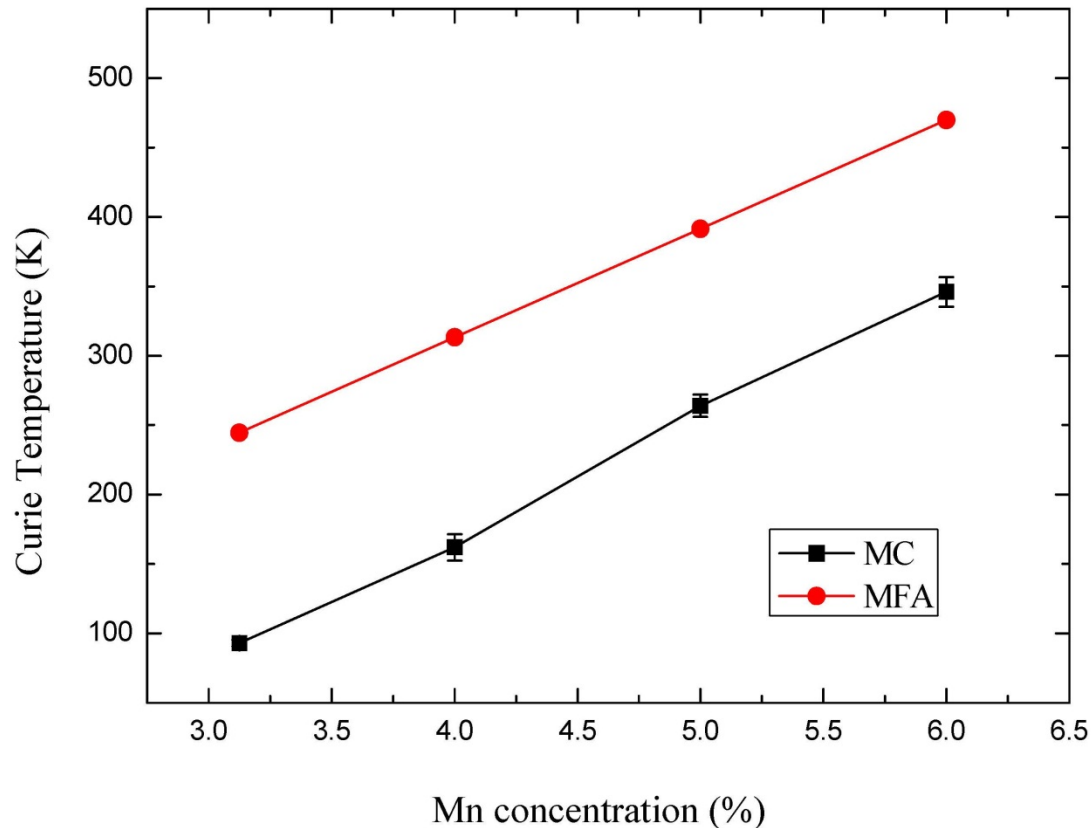
- Ideally, below T_c , U_4 is strictly equal to $2/3$, and above T_c , U_4 decays as T^{-1} .

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

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



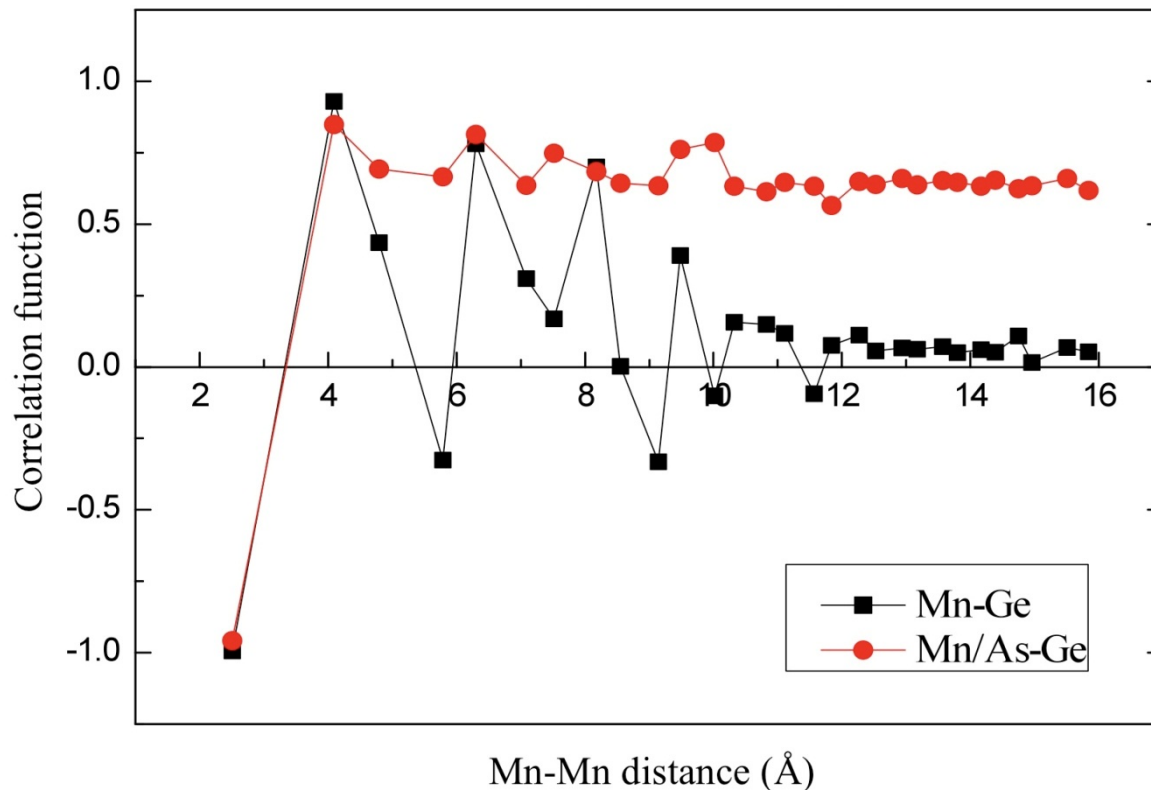
T_c from MC: linear with concentration



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 $T=0.01\text{K}$



A similar cumulant crossing approach yield a spin-glass phase transition temperature of $\sim 5\text{K}$ for 5% Mn



Concluding Remarks

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