

# First Principles Electronic Structure of Diluted Magnetic Semiconductors with high Curie Temp

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**Support: CSIR, DST**

# Outline of the Talk

- Electronic Structure of DMS material
- Oxide based DMS material
  - (i) Experimental Results
  - (ii) Theory
- DMS based on half Heusler
  - (i) Theoretical Prediction
  - (ii) Experimental Results
- Conclusions

# Spintronics

***Spin-based Electronics*** *i.e.* Exploiting electron's spin (over and above its charge ) to carry information → new generation of devices with new functionality.

***Spintronics Devices*** expected to have significant improvements in terms of **size, speed, information density, power consumption, nonvolatility etc.**

**Major Challenges:**

**Spin-injection**

**Spin-transport**

**Spin-coherence**

**Spin-detection....**

# Diluted Magnetic Semiconductors

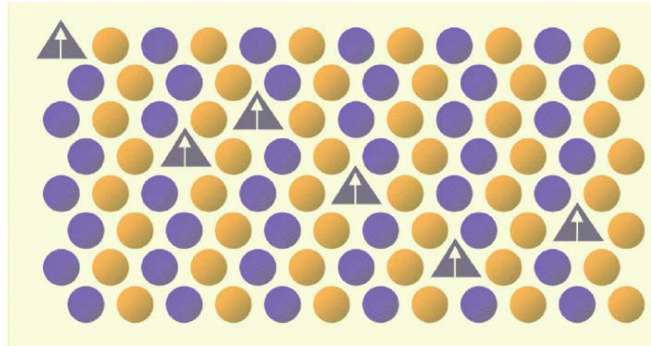
**Semiconducting Material  $\leftrightarrow$  Ferromagnetic Material**

**DMS: Semiconductors doped with TM impurities shows intrinsic ferromagnetism *eg.* ferromagnetism in Mn-doped GaAs (Ohno 1998)**

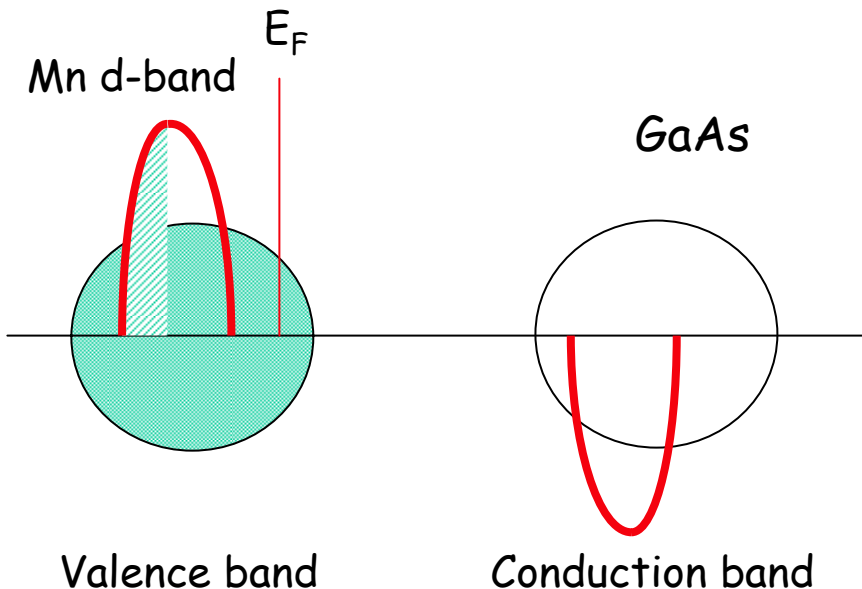
**Spin injection from a ferromagnetic metal to a semiconductor is difficult due to huge conductivity mismatch , whereas DMS spin-injector is advantageous from the point of view of an all semiconductor device.**

# Carrier-mediated ferromagnetism

## III-V DMS (MnGaAs)



*Mn = local moments + holes*  
*Mn<sup>3+</sup> → Mn<sup>2+</sup> + holes → act as source of*  
*localized spins 5/2 + effective mass acceptors*



$$H = \int d^3 r JS(r) \cdot s(r)$$

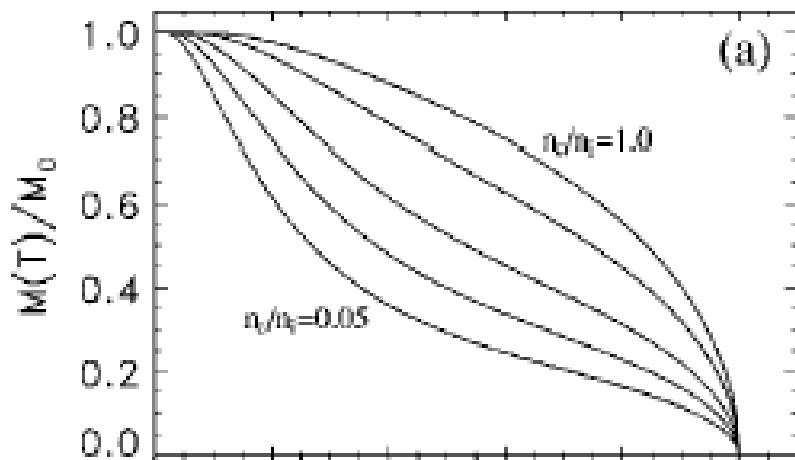
$S(r) \rightarrow$  Mn spin,  $s(r) \rightarrow$  hole spin

# Mean Field theory for ferromagnetism

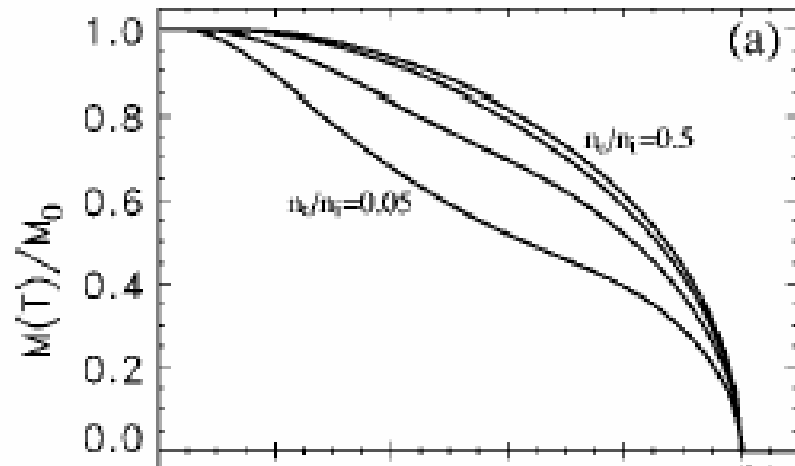
Das Sarma et al. PRB 2003

$$H = \int d^3r J(r) S(r) \cdot s(r)$$

## Temp. dependent magnetization



**Insulating DMS**



**Metallic DMS**

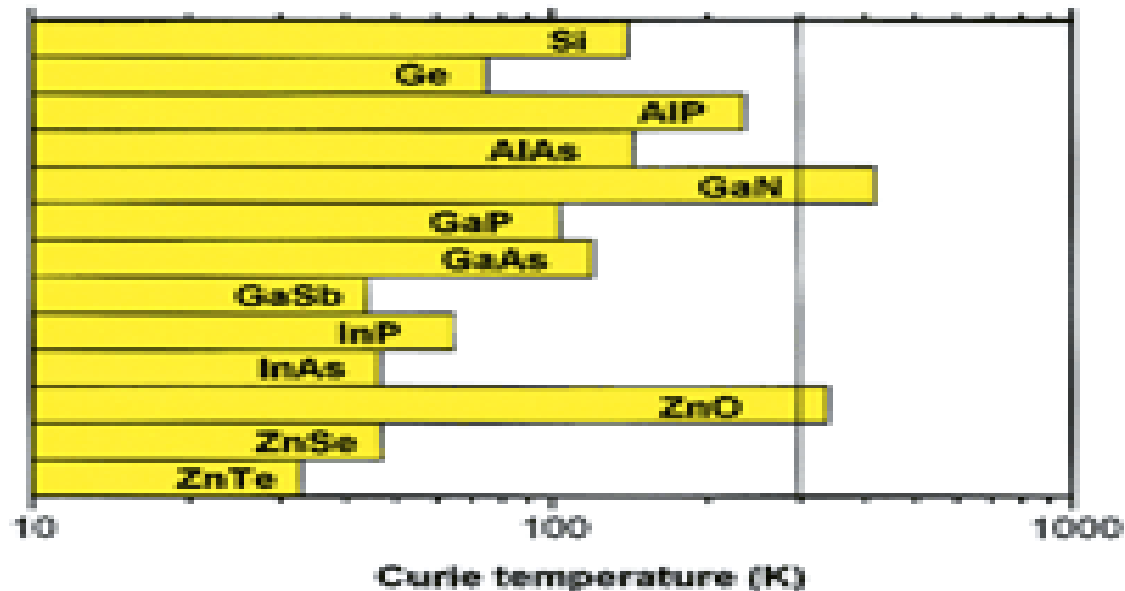
**Insulating ferromagnetic DMS exhibit non-mean-field like concave M(T) curves**

$n_i \rightarrow$  magnetic dopants,  $n_c \rightarrow$  holes in the host  $n_c/n_i \ll 1$

# Diluted Magnetic Semiconductors

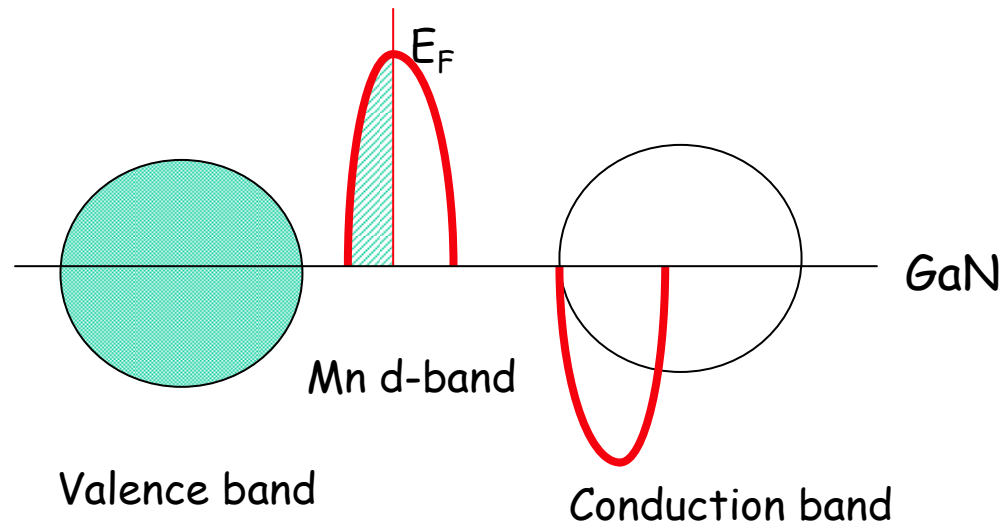
- Mn doped GaAs is a prototype DMS however the highest Curie temperature is 170K due to the limited solubility of Mn in GaAs and the presence of compensating defects giving rise to AFM in the system.

*Dietl et al.'s prediction*



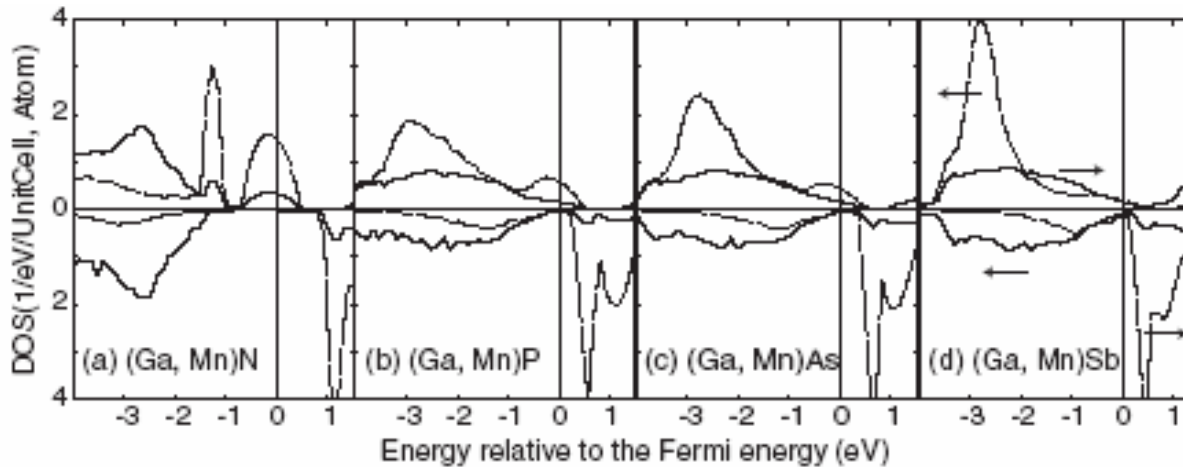
# Schematics Mn doped GaN

Impurity band forms in the gap, ferromagnetism is mediated by **Double Exchange**



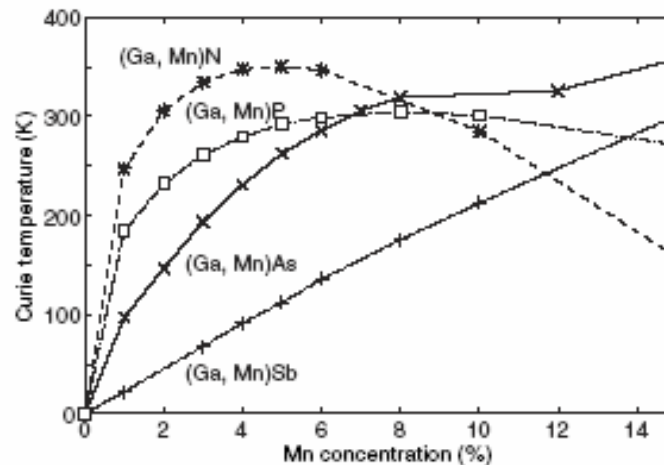
**Expt Scenario: More controversy than consensus**

# DMS and First Principle Calculations



In the series Mn doped GaN  $\rightarrow$  GaP  $\rightarrow$  GaAs  $\rightarrow$  GaSb the hole generated by introducing Mn in GaN have significant 3d character, while in GaSb the hole is of the host character.

Mean Field Curie Temp



Sato *et. al* JPCM, 2004

# Magnetism in ZnO

□ A comparison of thin films and bulk studies suggest that report of magnetism might not be intrinsic. The presence of carriers, particularly holes are crucial to mediate ferromagnetism.

□ Recent reports suggests ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides ( $\text{Al}_2\text{O}_3$ , ZnO,  $\text{SnO}_2$  ...). The origin of ferromagnetism may be due to the ex. int. between localized electron spin moments resulting from defects (oxygen vacancies) at the surfaces of nano particles.

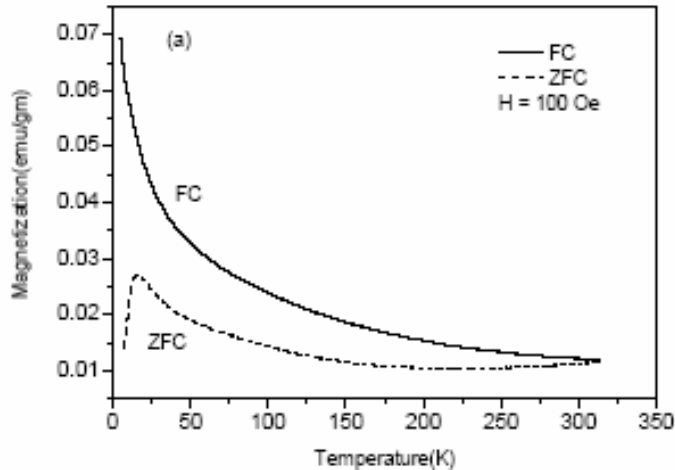
A.Sundaresan et. al. PRB 74 161306 (2006)

**Defects are crucial for magnetism in oxides**

# Fe doped ZnO Nanocrystals Expt.

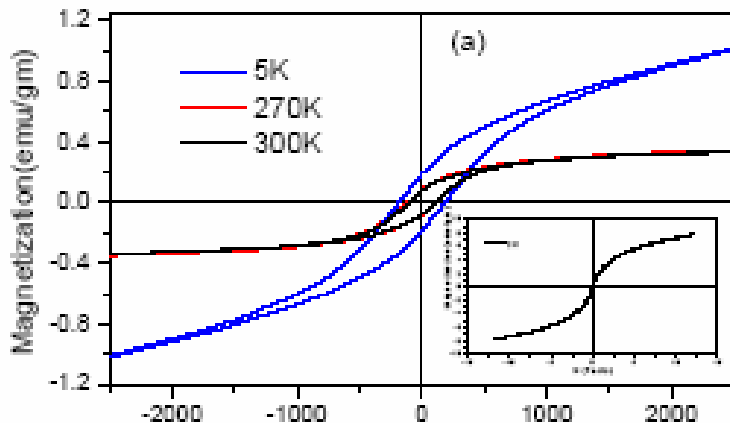
D. Karmakar et. al PRB (2007)

Non mean-field, low carrier density, localized carriers



Magnetization  $\rightarrow$  high ferromagnetic transition temp.

Local probes (EPR, Mossbauer)  $\rightarrow$  presence of Fe in both valence  $\text{Fe}^{2+}$  &  $\text{Fe}^{3+}$  indicating



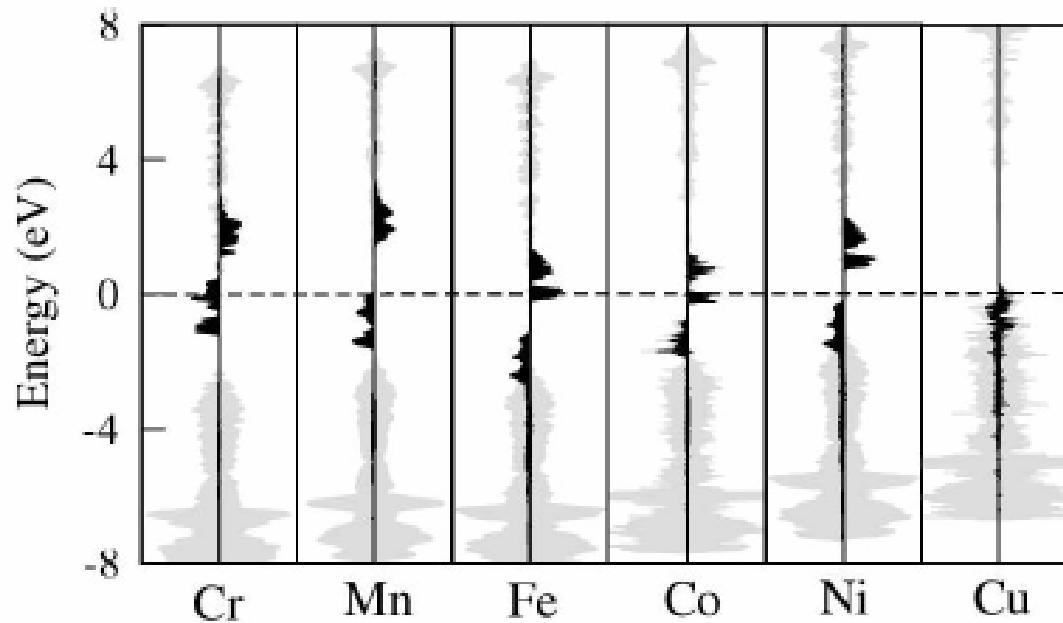
(i) Hole doping by Zn vac.

(i) Presence of minute segregated impurity phases like spinel ferrites.

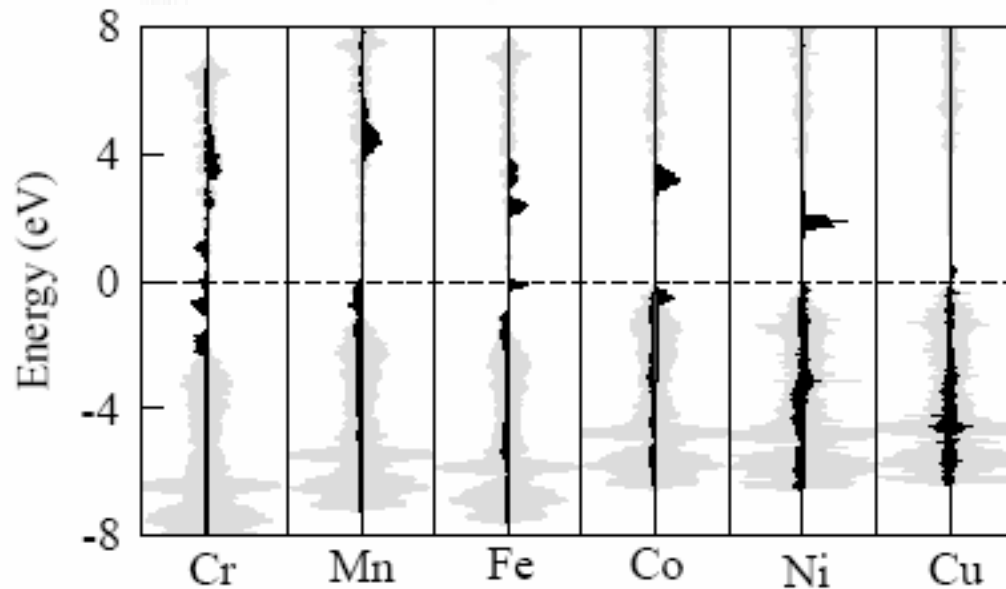
# Fe doped ZnO Theory

P. Gopal and N Spaldin, PRB, (2006)

**LDA**

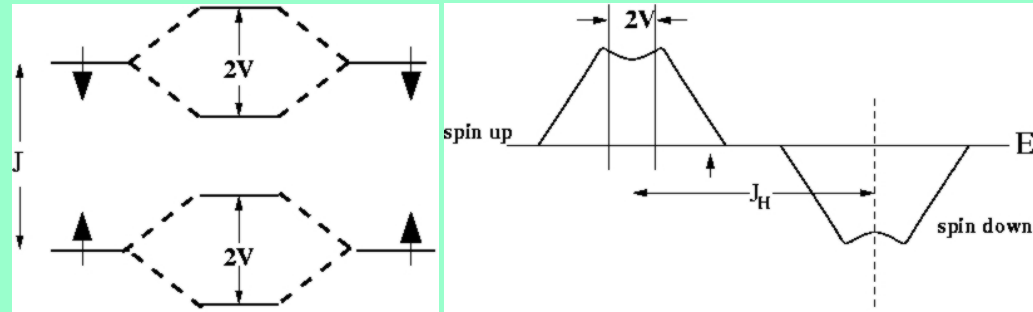
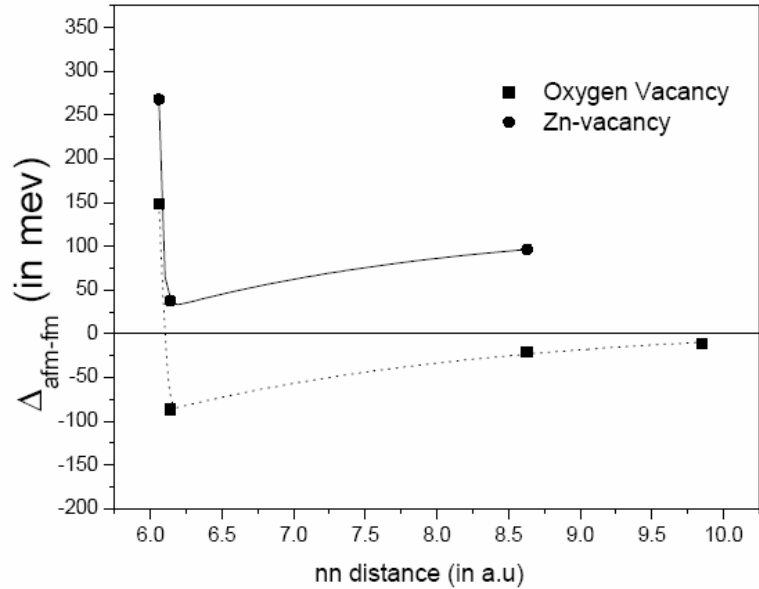


**LDA+U**



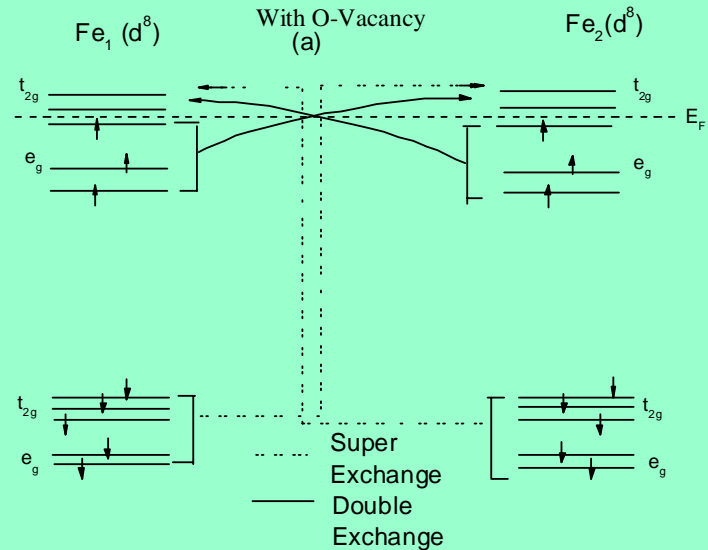
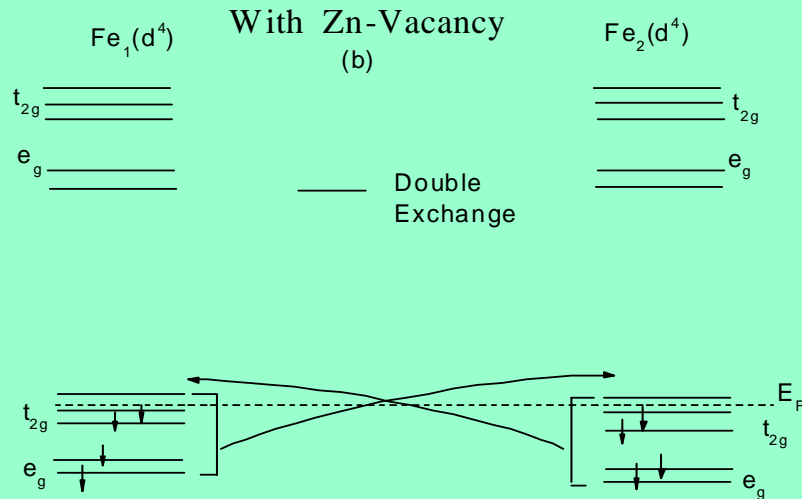
# Fe doped ZnO Theory

D. Karmakar et. al preprint (2006)



$$E = \pm \sqrt{(\Delta^2 \pm 2JV)}$$

$$= \pm J \pm V$$



# Diluted Magnetic Semiconductors

- ❑ Transition metal doped oxides (ZnO and TiO<sub>2</sub>) are promising candidates but exchange interaction is most probably mediated by native defects which are difficult to control in experiment.

**Current research in spintronics is directed toward an extensive search for potential DMS hosts with high Curie temperature.**

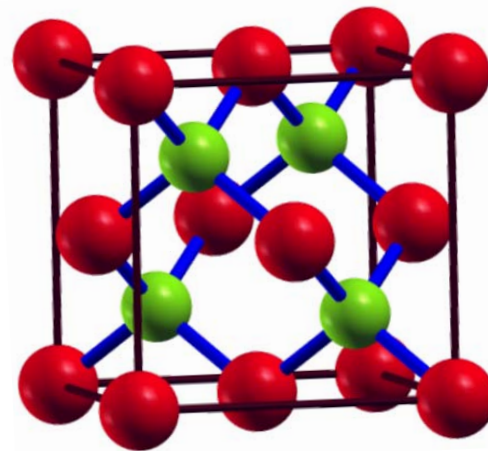
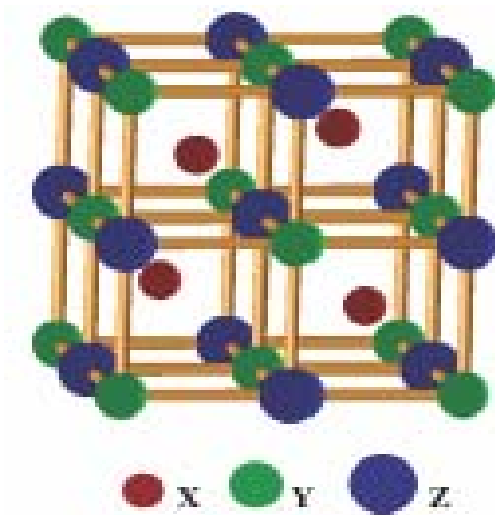
# **Diluted Magnetic Semiconductors based on half-Heuslers as hosts**

# Half-Heusler Compounds (XYZ)

The unit cell is fcc lattice with three atom as basis.

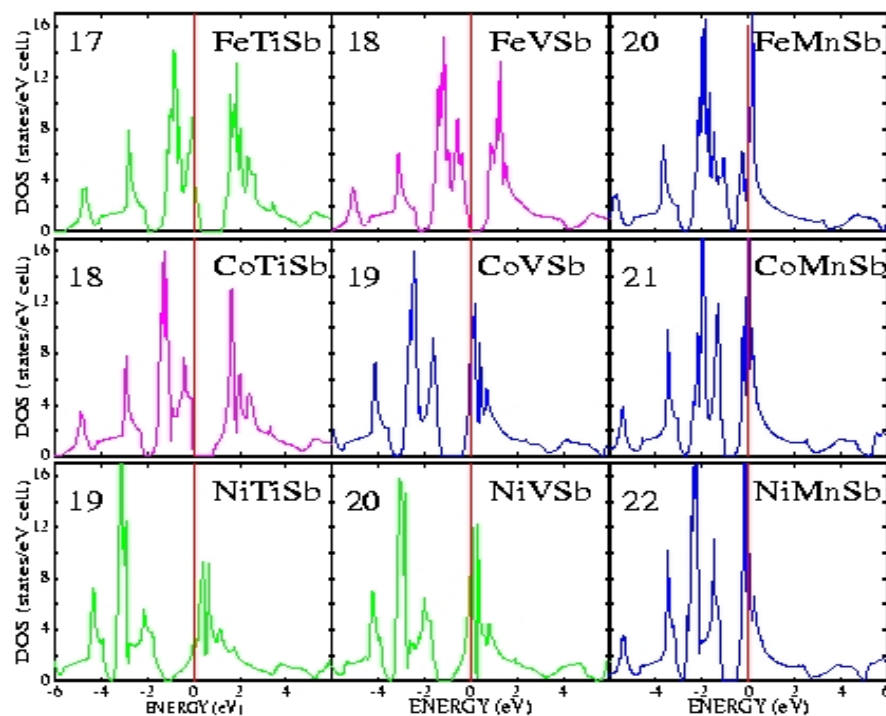
|           |          |           |           |           |           |           |           |           |
|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 22        | 23       | 24        | 25        | 26        | 27        | 28        | 50        | 51        |
| <b>Ti</b> | <b>V</b> | <b>Cr</b> | <b>Mn</b> | <b>Fe</b> | <b>Co</b> | <b>Ni</b> | <b>Sn</b> | <b>Sb</b> |
| Titanium  | Vanadium | Chromium  | Manganese | Iron      | Cobalt    | Nickel    | Tin       | Antimony  |
| 47.867    | 50.9415  | 51.9961   | 54.938049 | 55.845    | 58.933200 | 58.6934   | 118.710   | 121.760   |

← **Y** → ← **X** → **Z**



- The Zinc Blende structure adopted by semiconductors like GaAs, ZnSe, InAs. A = Ga, B = Empty, C = As, D = EMPTY.
- Heusler Alloys ⇒ Compatible with semiconductor technology.

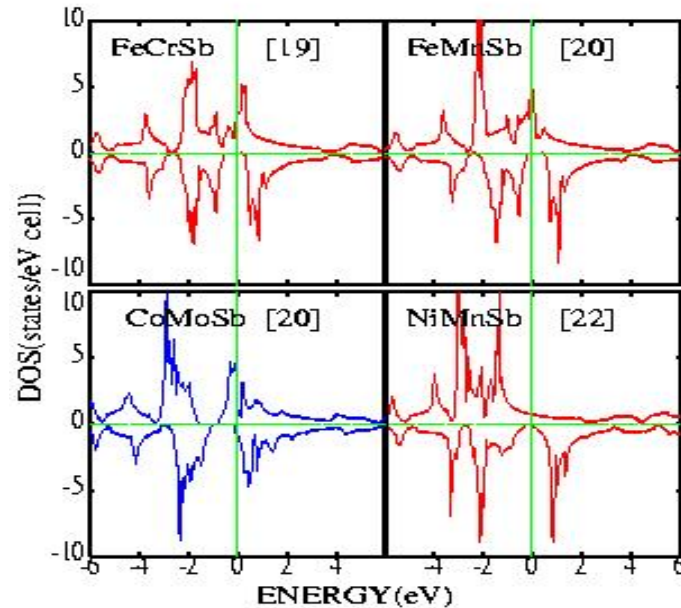
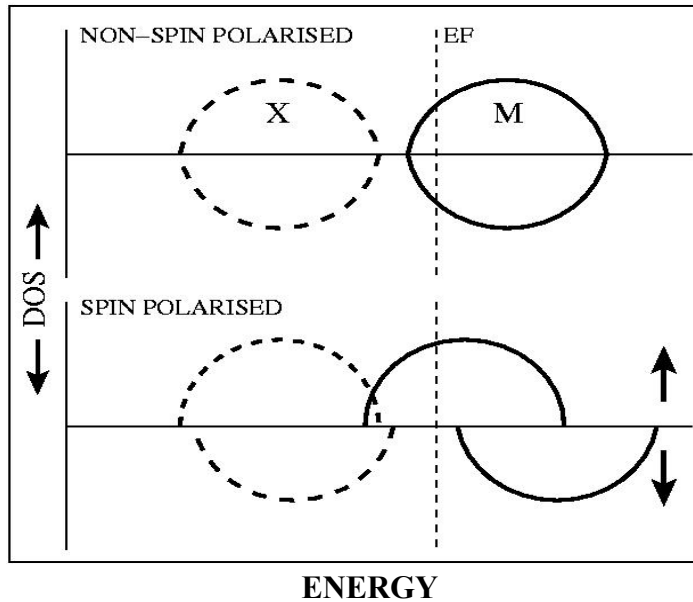
# LDA-LMTO Electronic structure Results: Spin integrated DOS of half-Heusler compounds



*Ref. Electronic structure and magnetism  
in half-Heusler compounds  
B.R.K. Nanda and I. Dasgupta  
J. Phys.: Condensed Matter  
15, 7307-7323 (2003)*

- **Key Results:** A gap close to the Fermi level.  
VEC = 18 Compounds are semiconductors.  
VEC > 18 Compounds may be half-metallic ferromagnets.

# VEC > 18 and Spin-Polarization



- **Ferromagnetism: Competition between BETWEEN**  
⇒ (i) Kinetic energy, (ii) Coulomb repulsion
- **Gap in the DOS is important for half-metallic ferromagnetism.**

*Ref. Electronic structure of half-metallic magnets  
B.R.K. Nanda and I. Dasgupta  
Comp. Mat. Science, 2006*

# Doped Semiconducting half-Heusler compounds

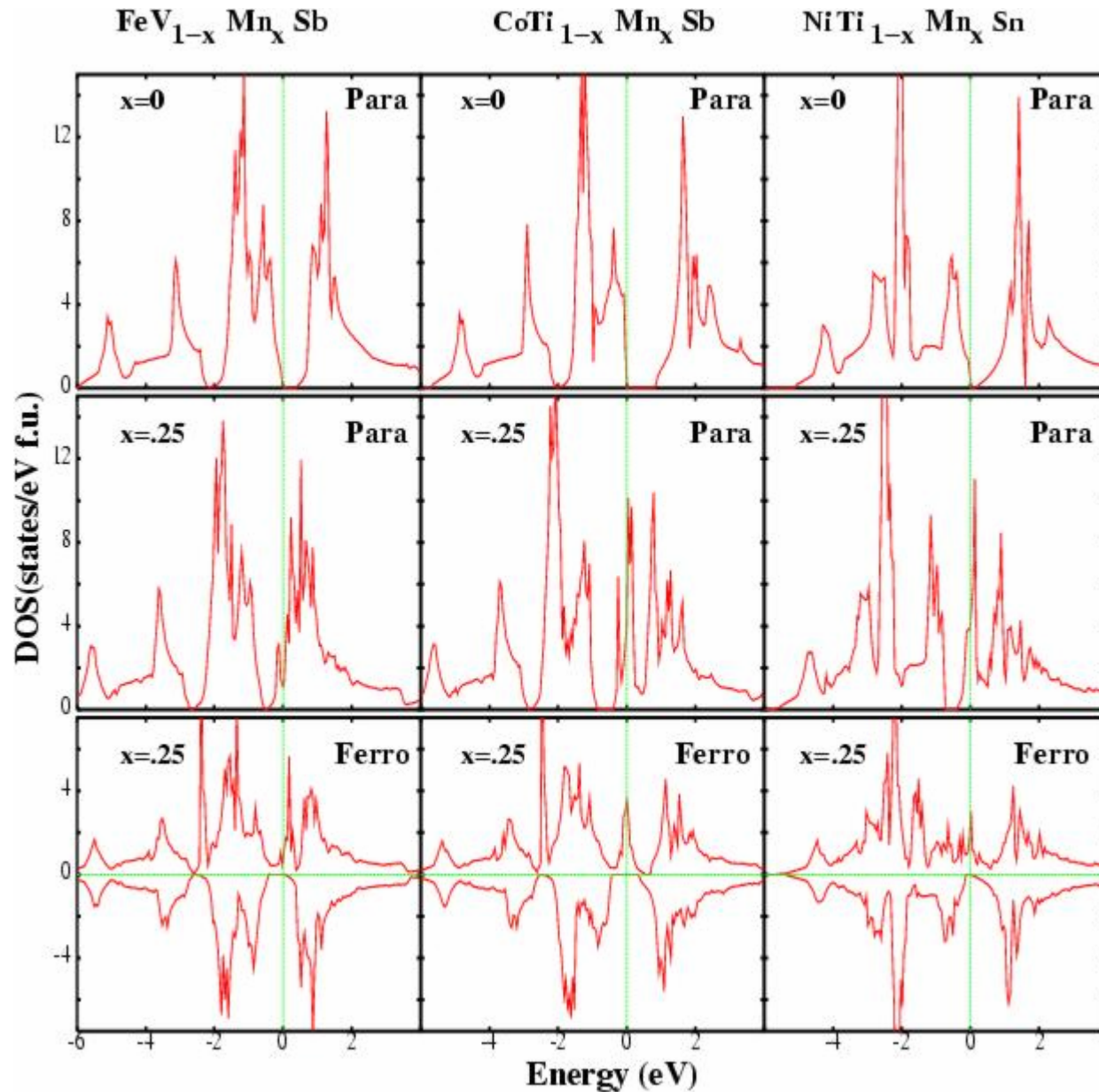
- **Why doped half-Heuslers ?**

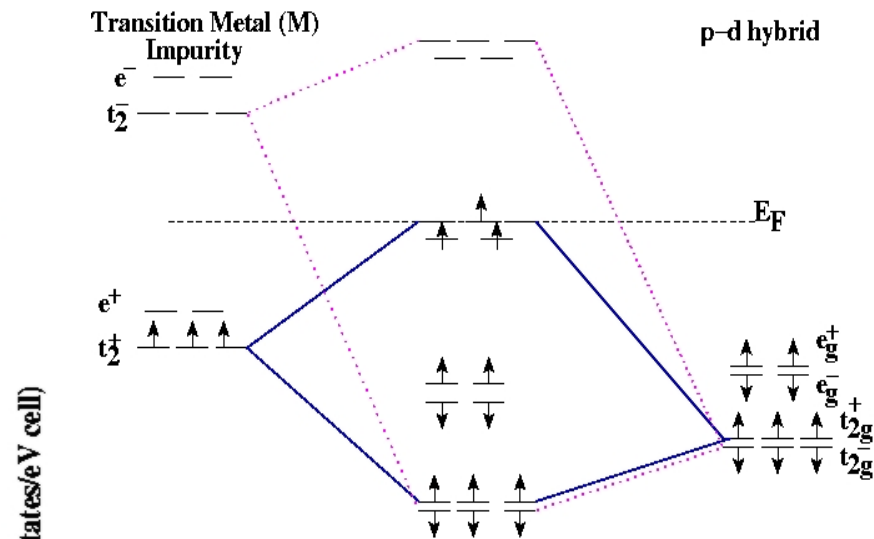
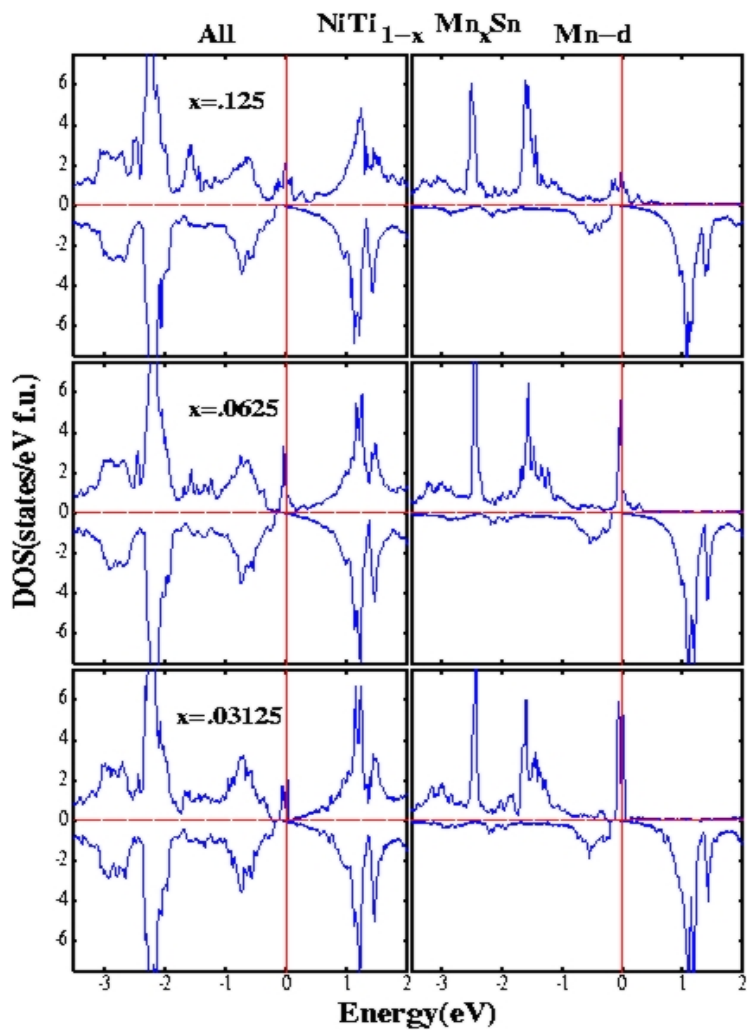
- **Half-Heusler compounds with 18 valence electrons are semiconductors. (e.g. FeVSb, CoTiSb, NiTiSn). ⇒ Doping of Mn/Cr at V/Ti sites will make the number of valence electrons more than 18.**

- **Structural similarity between the half-Heusler compounds and DMS.**

**Are doped half-Heusler compounds magnetic ?**

# Doped Half-Heusler Systems:

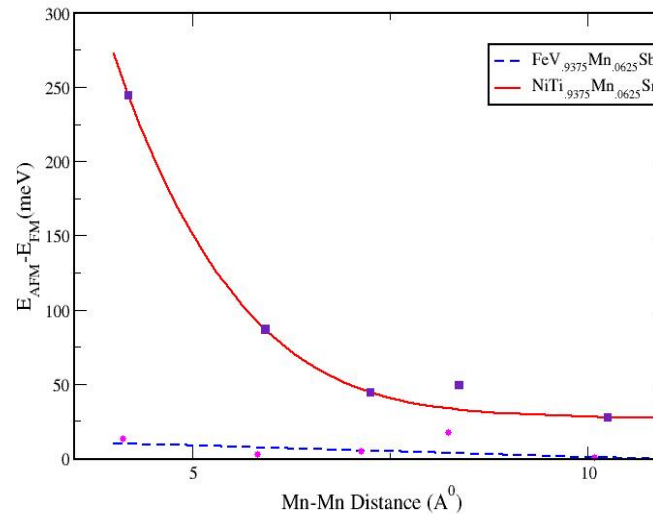
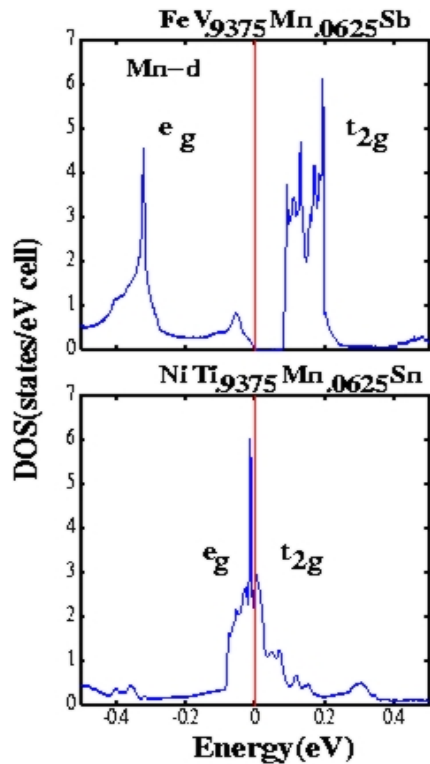




- **XYZ (VEC=18) ⇒ semiconducting.**
- Doped system ⇒ X(Y,Mn)Sb (VEC>18) half-metallic**

*Ref. Electronic Structure and magnetism in doped semiconducting half-Heusler compounds, B.R.K. Nanda and I. Dasgupta  
 J. Phys: Condensed Matter 17 5037 (2005)*

# Exchange Interaction in Supercell Calculation



**Short Range Interaction**

**Exponentially damped due to Half metallicity**

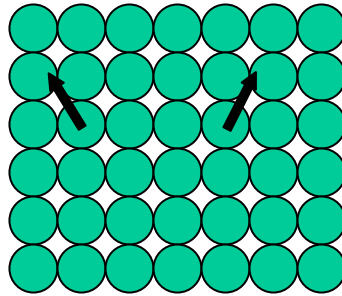
**Mn cluster within short radial distance → Magnetic Percolation**

# Disorder

KKR-CPA calculations : configuration averaging, calculation of Heisenberg pair-exchange parameters using methodology of Liechtenstein *et al.*

Classical Heisenberg Hamiltonian

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



$$J_{ij} = \frac{1}{4\pi} \int_{E_F} dE \operatorname{Im} \{ \operatorname{Tr}_L (\Delta_i T_{\uparrow}^{ij} \Delta_j T_{\downarrow}^{ji}) \}$$

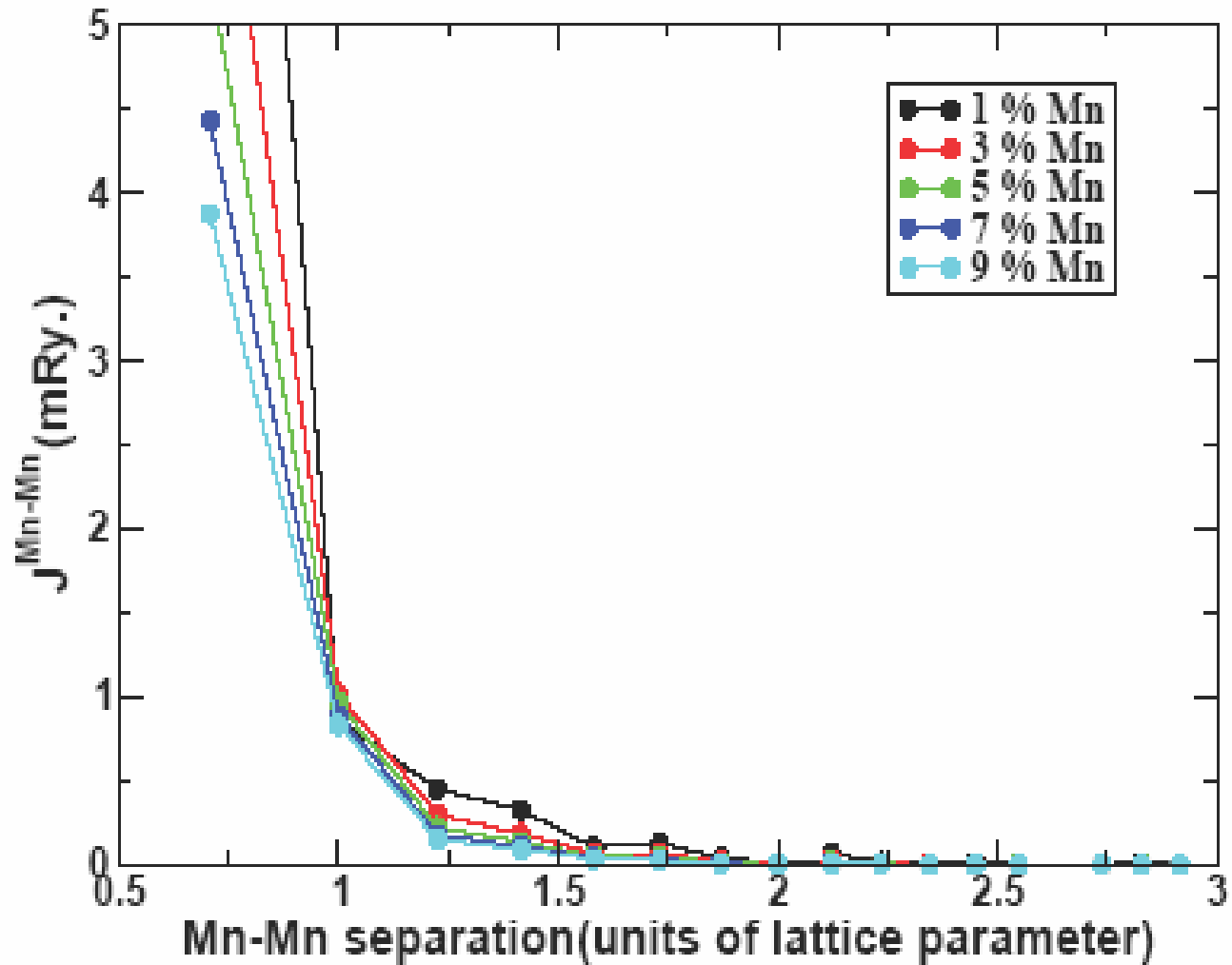
where,

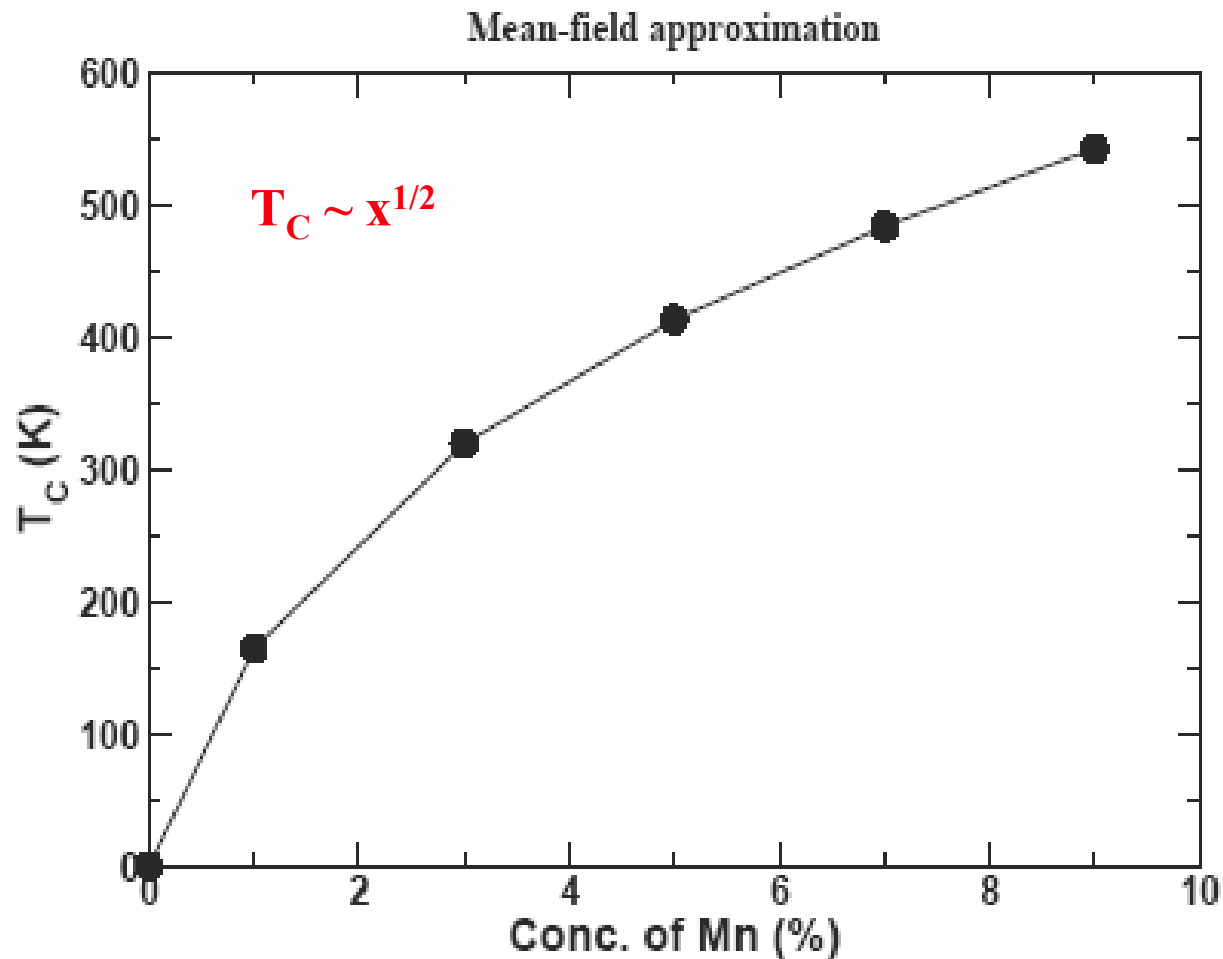
$$\Delta_i = t_{i\uparrow}^{-1} - t_{i\downarrow}^{-1}$$

$t$  : on-site scattering matrix

$T$  : scattering path operator

# Exchange interaction with disorder (CPA)



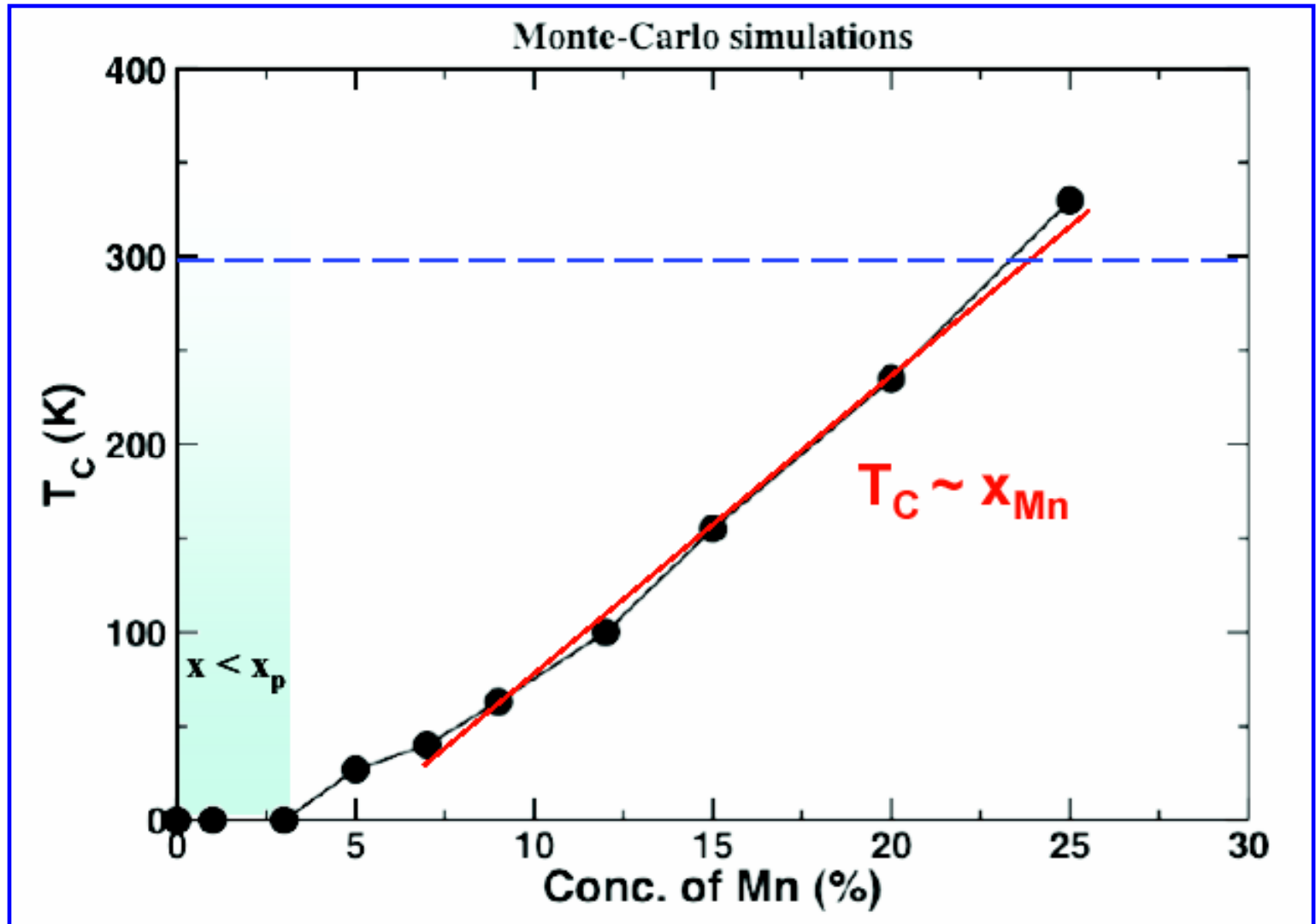


Double exchange : FM is favorable

TB model :-

$$\langle W^2 \rangle_{conf} = \sum_{j \neq 0} \langle |H_{0j}|^2 \rangle = x \sum_{j \neq 0} |t_{0j}|^2$$

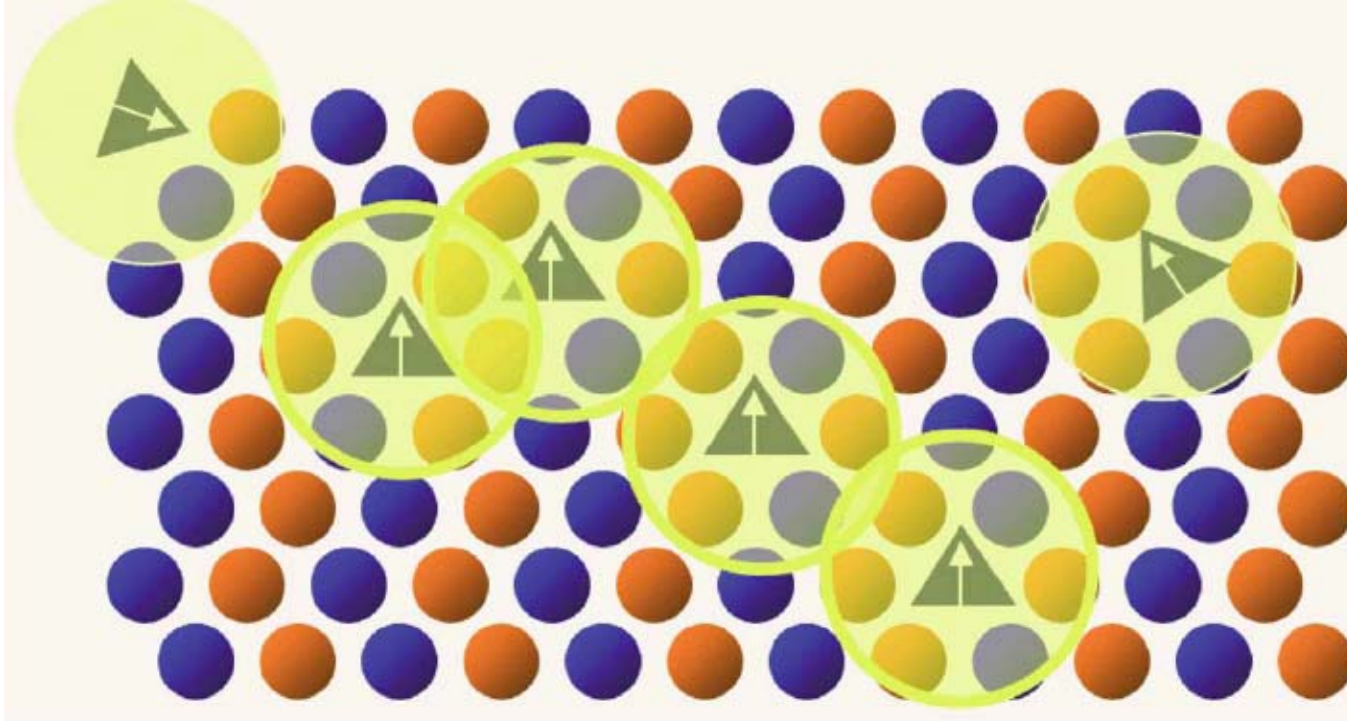
# Monte- Carlo Simulations



Ferromagnetism in Mn doped half-Heusler NiTiSn: Theory and experiment,  
B. Sanyal et. al. Appl. Phys. Lett. 89, 212502 (2006)

# Magnetic Percolation

Kaminski and Das Sarma, PRL'2002



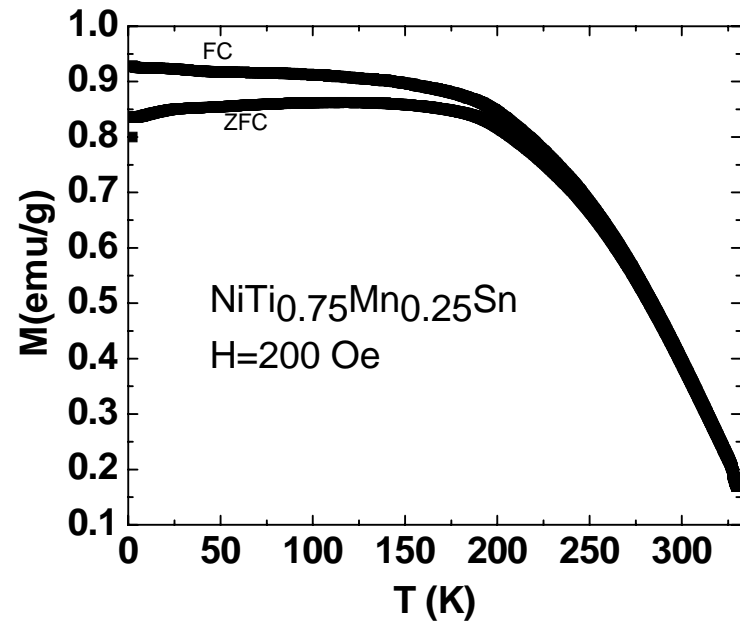
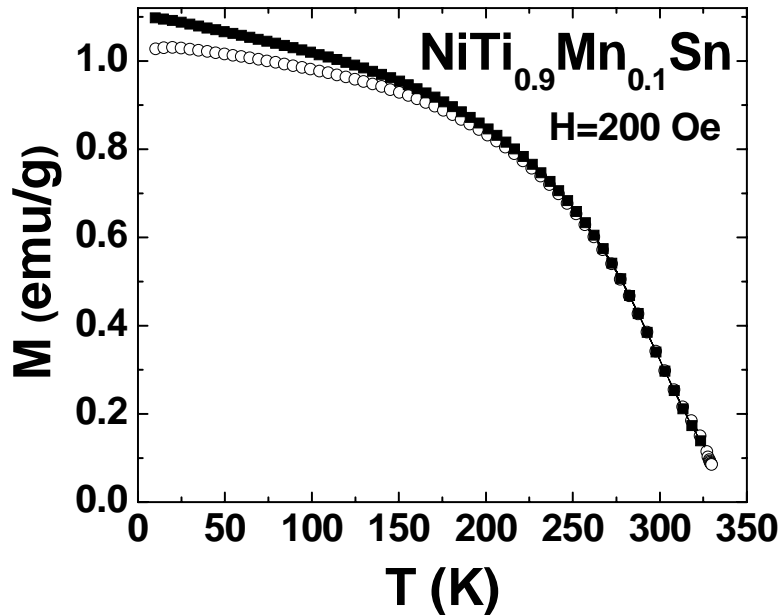
$x \geq x_c \rightarrow$  Long range Ferromagnetism

May explain ferromagnetism in doped Heusler and oxide based DMS. Defects and sample growth conditions may play important role.

# $T_c$ in DMS :

|                | $(\text{Ga}_{1-x}\text{Mn}_x)\text{As}$ | $(\text{Ga}_{1-x}\text{Mn}_x)\text{N}$ |        | $\text{Ni}(\text{Mn}_x\text{Ti}_{1-x})\text{Sn}$ |        |
|----------------|---|--|--------|--|--------|
|                | X=0.05                                  | X=0.05                                 | X=0.08 | X=0.03   | X=0.15 |
| MFA            | 280                                     | 376                                    | 376    | 250  | 620    |
| MC<br>(Random) | 137                                     | 55                                     | 90     | 0  | 200    |
| Expt           | 45-118                                  | 0-370                                  | 0-370  | ?  | ?      |

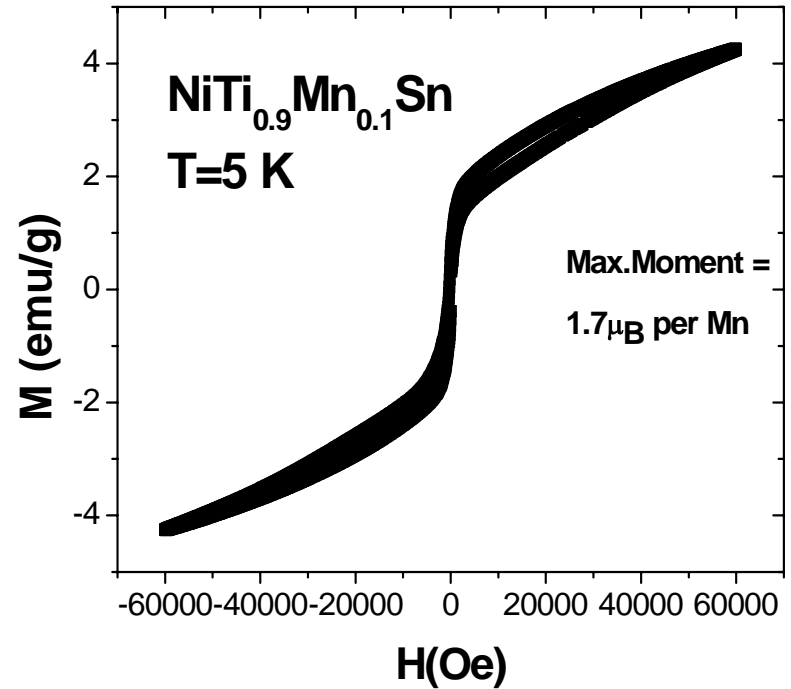
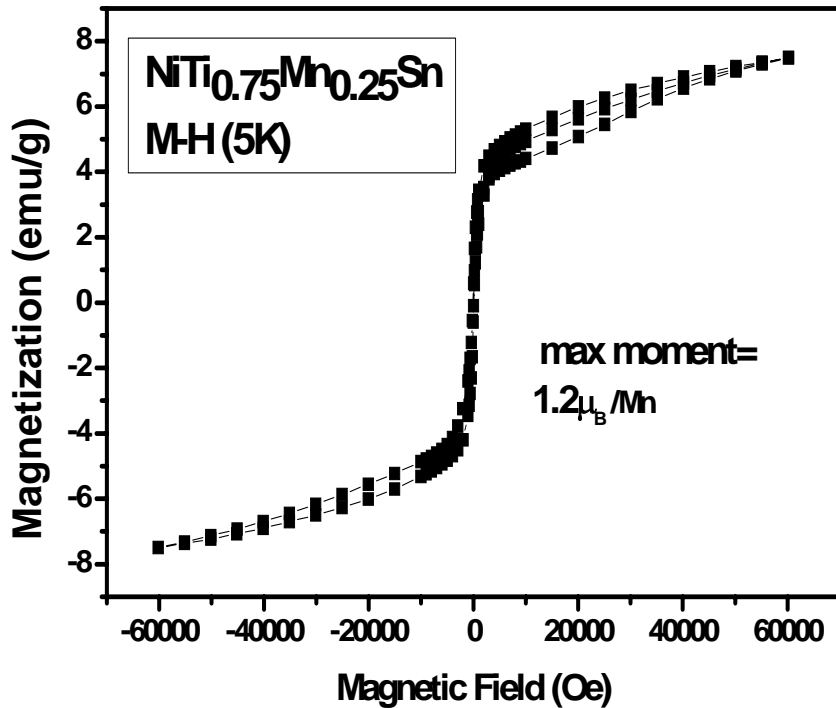
# Experimental Signature of ferromagnetism: Temperature dependence of magnetization of $\text{NiTi}_x\text{Mn}_{1-x}\text{Sn}$



K. G. Suresh et al.

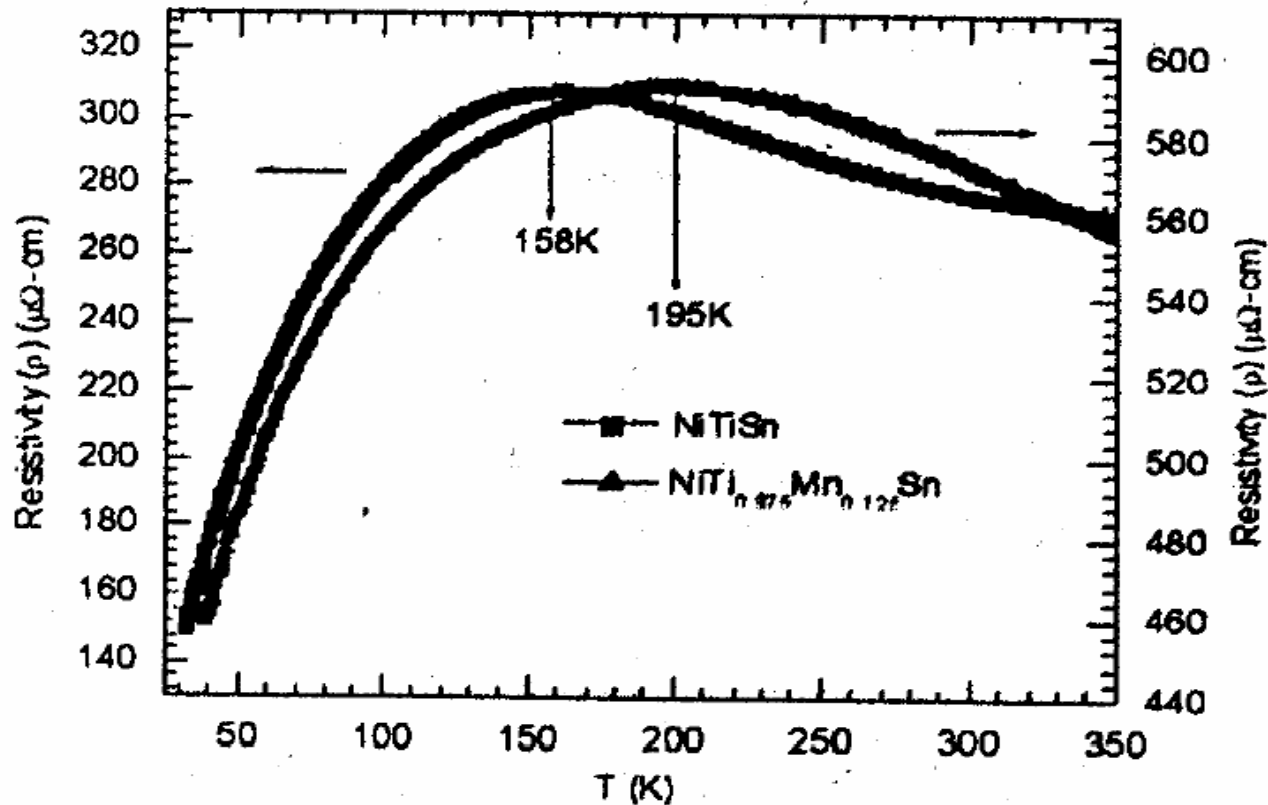
**M vs T curve has a typical mean field shape → ferromagnetism is driven by itinerant carriers.**

# Experimental Signature of Ferromagnetism



M-H plots of NiTi<sub>0.75</sub>Mn<sub>0.25</sub>Sn and NiTi<sub>0.9</sub>Mn<sub>0.1</sub>Sn

# Transport Data



Samples are metallic, however bad metal with relatively high resistivity.

K.J.S Sokhey, S.B. Roy and A.K. Nigam, Proceedings of the DAE Solid State Physics Symposium, (2005)

## Diluted magnetic semiconductors with high Curie temperature based on $C1_b$ compounds: $\text{CoTi}_{1-x}\text{Fe}_x\text{Sb}$

Kristian Kroth, Benjamin Balke, Gerhard H. Fecher,<sup>a)</sup>

Vadim Ksenofontov, and Claudia Felser<sup>b)</sup>

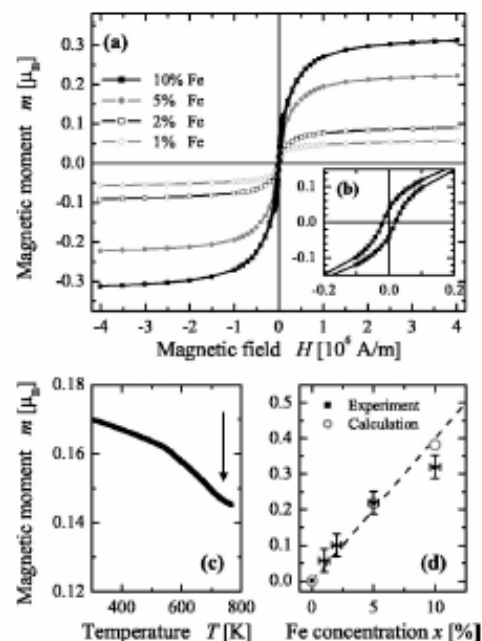
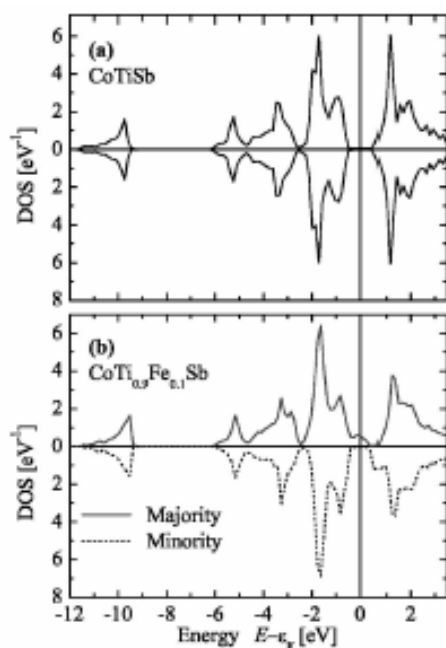
*Institut für Anorganische und Analytische Chemie, Johannes Gutenberg—Universität, D-55099 Mainz, Germany*

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(Received 8 June 2006; accepted 13 October 2006; published online 15 November 2006)

Diluted magnetic semiconductors were prepared by substituting titanium in the semiconducting compound  $\text{CoTiSb}$  with iron. The structural, electronic, and magnetic properties of the pure and doped materials were investigated. It was found that substitution of up to 10% Ti by Fe does not affect the crystalline structure. Self-consistent calculations of the electronic structure predict the material to be a half-metallic ferromagnet. The Curie temperature of the Fe substituted alloy is far above room temperature ( $>700$  K), thus making that material a serious candidate for future electronic applications, in particular, for magnetoelectronics and spintronics. © 2006 American Institute of Physics. [DOI: 10.1063/1.2388876]



## Summary

- ❖ Calculations predict magnetic impurities (e.g. Mn ) in semiconducting half-Heusler systems like NiTiSn may lead to half-metallic ferromagnetism with possibly high Curie temperature.
- ❖ Mechanism magnetic percolation