Electronic Structure of Novel Magnetic Systems: Insights from Spin Polarized DFT Calculations

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Monami

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Plan of the Talk

Introduction

Stoner Model of Ferromagnetism

- Electronic structure of Half-metallic ferromagnets

Exchange Mechanism

- Half Heusler based Diluted Magnetic Semiconductors
- Magnetism in Type-1 Clathrates

Hamiltonian

$$H = \sum_i [-\frac{1}{2}\Delta_i^2 + V(r_i)] + \sum_{i<j} \frac{e^2}{|r_i - r_j|}$$

Find some complete one-particle basis:

$$H = \sum_i \varepsilon_i n_i + \sum_{i \neq j} t_{ij} c_i^+ c_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} c_i^+ c_j^+ c_l c_k$$

↓ **Kinetic Energy**

↓ **Electron-electron int.**

The tendency toward magnetism is determined by a competition between exchange and kinetic energy effects

Magnetism

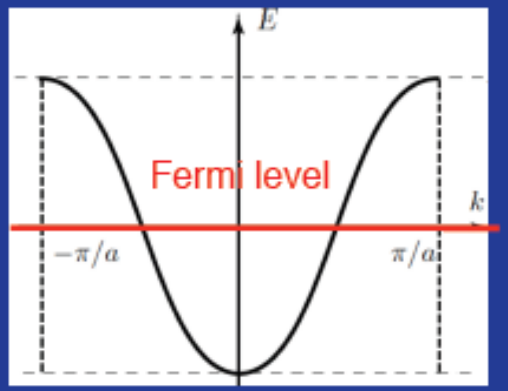
Two key energy scales: **t and U**

t: *hopping amplitude of electron between atoms*

U: *on-site repulsive interaction → cost of a double occupancy*

$$H = -t \sum_{\langle ij \rangle} (c_i^\dagger c_j + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

U << t : A metal (itinerant state)
Band picture OK
1 electron/site → ½-filled band



Broad energy bands electrons are highly itinerant –itinerant magnetism→ SDFT

U >> t An insulator
(motion blocked by repulsive interaction)

Narrow energy bands tendency toward localization → "see each other"

$$H_{Heis} = \sum J_{ij} S_i S_j$$

First Principles Electronic Structure Calculations: Foundations

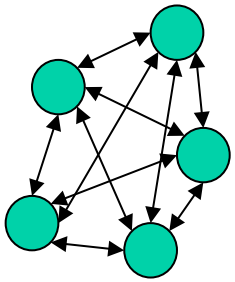
$$H\Psi = E\Psi$$

$$H = \sum_i [-\frac{1}{2}\Delta_i^2 + V(r_i)] + \sum_{i<j} \frac{e^2}{|r_i - r_j|}$$

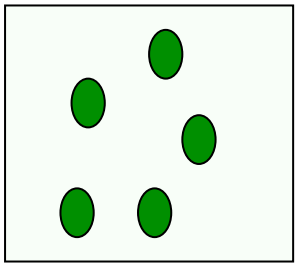
Noninteracting part **Interacting part**

- **Density functional theory → Kohn-Sham + Local density approximation (LDA)**

→ Reduction to an effective non-interacting system.



KOHN-SHAM APPROACH



KS-equation →

$$\left[-\frac{1}{2}\nabla^2 + V_H(n_{GS};\vec{r}) + V_{ext}(n_{GS};\vec{r}) + V_{xc}(n_{GS};\vec{r})\right]\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r})$$

← V_{eff} →

LSDA

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + V_{eff}^{\pm}(\vec{r}) \right] \phi_i^{\pm}(\vec{r}) = E_i\phi_i^{\pm}(\vec{r}) \qquad V_{xc}^{\pm}(\vec{r}) = \frac{\delta E_x[n^+(r), n^-(r)]}{\delta n^{\pm}(r)}$$

Stoner Model for Ferromagnetism

- **Quantitatively not accurate but captures the essential physics.**
- **Provide a framework to interpret results obtained from spin DFT.**

Electron density $n(\vec{r}) = n^{+}(r) + n^{-}(r)$

Magnetization density $m(\vec{r}) = n^{+}(r) - n^{-}(r)$

"Usually" $m(\vec{r})$ is a small parameter compared to density $n(\vec{r})$, expand $V_{xc}^{\pm}(\vec{r})$ in terms of $m(\vec{r})$

$$V_{xc}^{\pm}(\vec{r}) = V_{xc}^{0}(\vec{r}) \mp m(\vec{r})\tilde{V}(n(\vec{r}))$$

$V_{xc}^{0}(\vec{r}) \equiv$ Exchange-correlation potential for non-spin-polarized electrons.

The average value of $\tilde{V}(n(\vec{r}))$ is a positive so that more attractive potential acts on the majority electrons compared to minority electrons.

Stoner Model: $V_{xc}^{\pm}(\vec{r}) = V_{xc}^{0}(\vec{r}) \mp \frac{1}{2}IM$

The potential difference is now independent of $\vec{r}$.

$I \equiv$ the exchange integral $\equiv$ Stoner parameter and $M = \int_{\Omega} m(\vec{r}) d^{3}\vec{r}$

Stoner Model for Ferromagnetism

A constant change of the potential does not change the Kohn-Sham eigenfunctions, but eigenvalues shift by a constant amount.

$$\epsilon^{\pm}_{k\nu} = \epsilon^{0}_{k\nu} \mp \frac{1}{2} IM$$

Exchange splitting: $\epsilon^{+}_{k\nu} - \epsilon^{-}_{k\nu} = \Delta = IM$

$$n^{\pm}(E) = \Sigma_{\nu} \int_{BZ} \delta(E - \epsilon^{\pm}_{k\nu}) dk = n^{0}(E \pm \frac{1}{2} IM)$$

$n^{0}(E) \equiv$ DOS for a non magnetic system

No. of electrons,

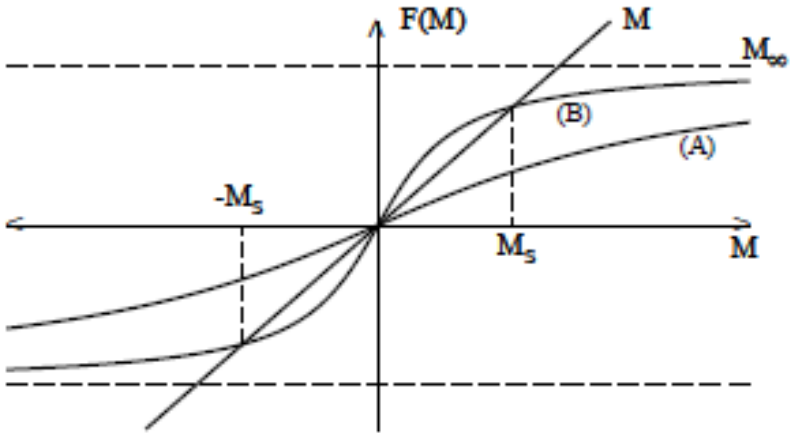
$$N = \int^{E_F} [n^{0}(E + \frac{1}{2} IM) + n^{0}(E - \frac{1}{2} IM)] dE$$

$$M = \int^{E_F} [n^{0}(E + \frac{1}{2} IM) - n^{0}(E - \frac{1}{2} IM)] dE$$

The moment can be determined by the equations M = F(M)

$$F(M) = \int^{E_F(M)} [n^{0}(E + \frac{1}{2} IM) - n^{0}(E - \frac{1}{2} IM)] dE$$

Graphical Soln:



$$F(M) = \int^{E_F(M)} [n^0(E + \frac{1}{2}IM) - n^0(E - \frac{1}{2}IM)]dE$$

Finite magnetization always exists, if $F'(M)|_{M=0} > 1$

$$F'(M) = \frac{I}{2}[n^0(E_F+\frac{1}{2}IM)+n^0(E_F-\frac{1}{2}IM)]+[n^0(E_F+\frac{1}{2}IM)-n^0(E_F-\frac{1}{2}IM)]\frac{dE_F}{dM}$$

$$F'(0) = I\ n^0(E_F)$$

The sufficient condition for ferromagnetism

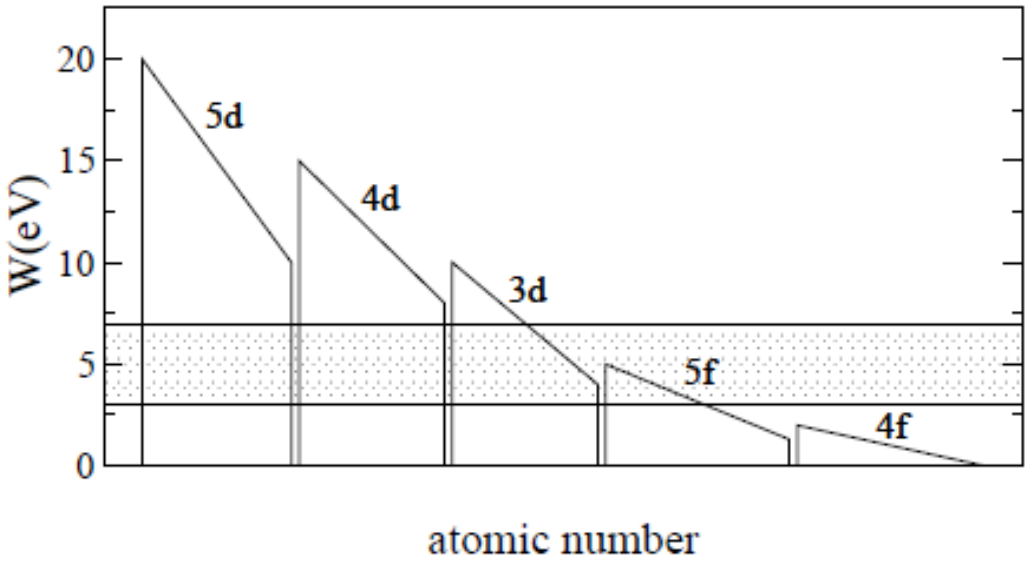
$$I\ n^0(E_F) > 1$$

The same result can be obtained starting from Hubbard model using mean field approximation.

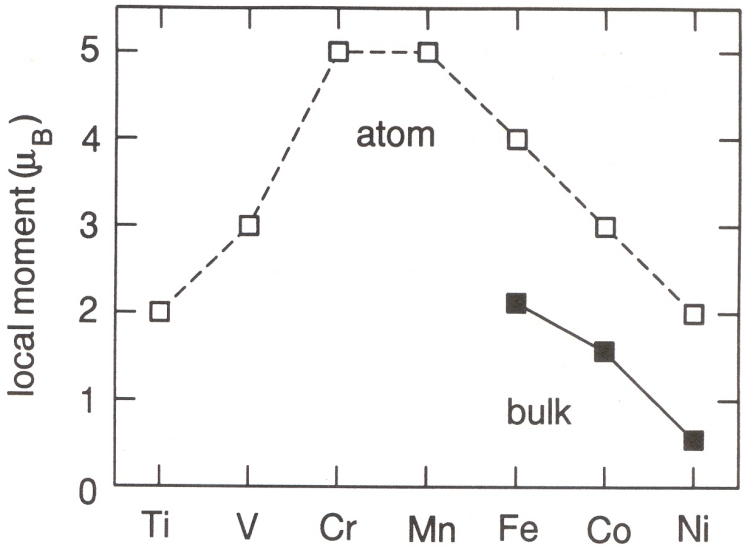
Stoner Criteria and Trends in Magnetism

$$I\ n^0(E_F)\ >\ 1$$

- I is an intra-atomic, element specific and independent of local environment $I_{3d} > I_{4d} > I_{5d}$
- $n^0(E_F)$ → co-ordination number and hopping matrix elements. $n^0(E_F) \sim n_d{}^0(E_F) \sim 1/W_d$ → $W_{3d} < W_{4d} < W_{5d}$



Stoner Model and Ferromagnetism



Local magnetic moments of isolated 3d atoms→ Hunds's Rule

Metal	$n_0(E_F)$ [Ry^{-1}]	I[Ry]	$In_0(E_F)$
Na	6.2	0.067	0.42
Al	5.6	0.045	0.25
Cr	9.5	0.028	0.27
Mn	21	0.030	0.63
Fe	42	0.034	1.43
Co	27	0.036	0.97
Ni	55	0.037	2.04
Cu	3.9	0.027	0.11
Pd	31	0.025	0.78

Stoner Condition → Bulk Magnetism

Ref: R Zeller, Computational Nanoscience: Do it yourself 31, 419, 2006

Strongly Correlated Systems and LSDA

- Structural properties are well described so the overall charge density is well presented within LSDA, while the energy scale associated with the magnetic instability is not adequately treated in LSDA.
- In LSDA the localization is not controlled by the Hubbard U, but by a quantity which represents the Hund's rule exchange, the Stoner I. This I is an order of magnitude smaller than U (I ~ 1eV, U ~ 10eV)
- This is due to the homogeneous electron gas picture inherent in LDA, where the spin dependence has its origin in Hunds rule exchange , while in Mott insulators the Hubbard U is the driving force.
- **CURE: Hubbard U instead of Stoner I**
- **LDA+U method: Anisimov, Zannen and Andersen, PRB 44, 943 (1991)**

Electronic structure and magnetism in materials for spintronic application

(a) *Half Metallic Magnets*
(b) *Diluted Magnetic Semiconductors*

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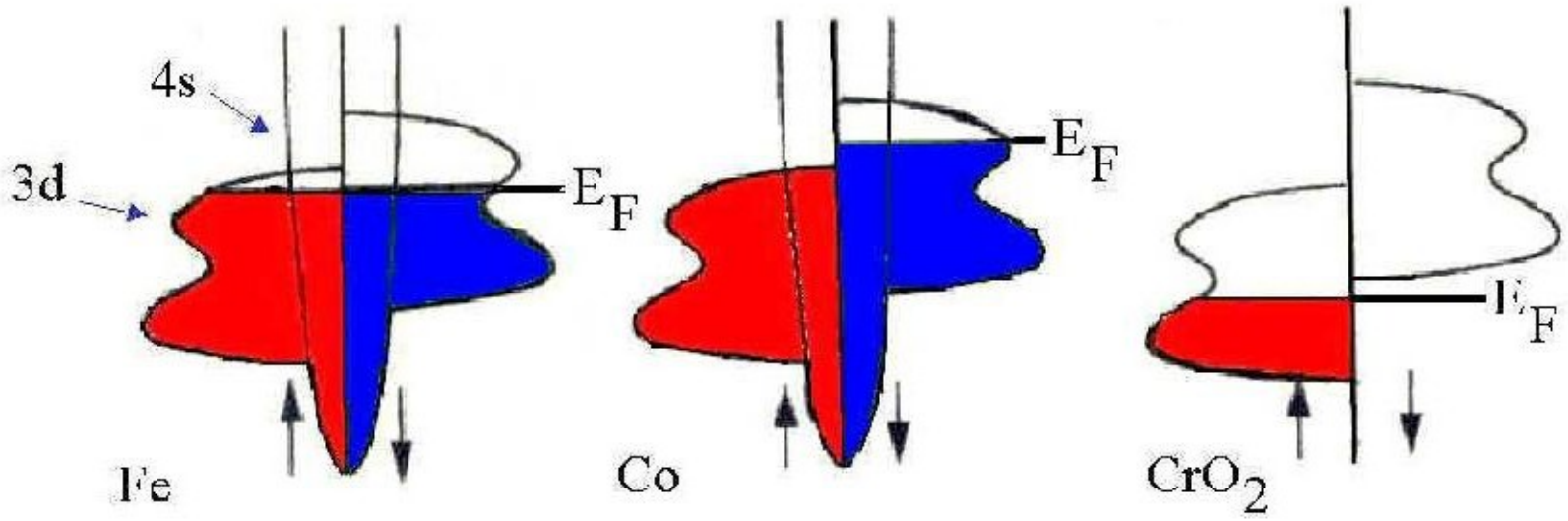
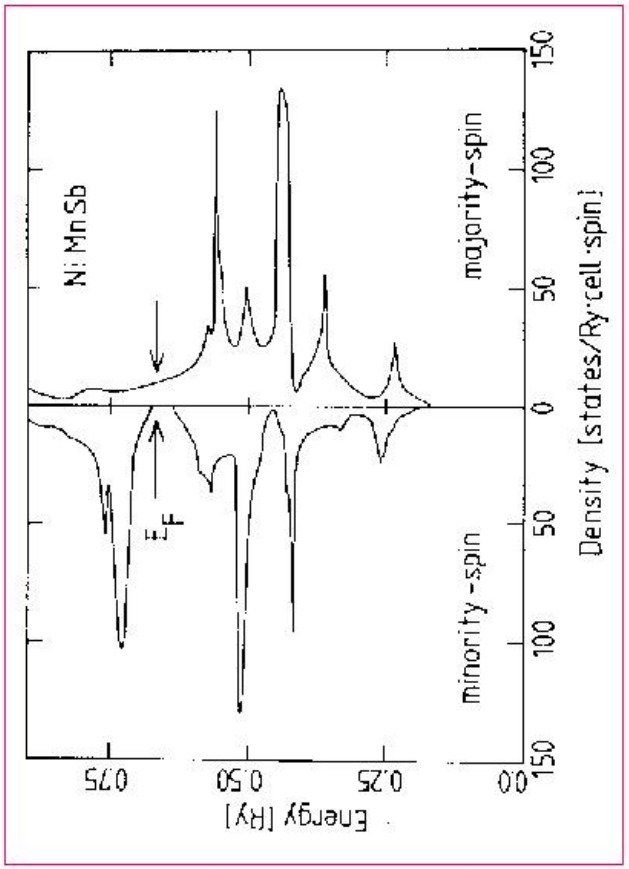
Spin-based Electronics ***i.e.*** **Exploiting electron's spin (over and above its charge) to carry information → new generation of devices with new functionality.**

Half Metals
(Half Metallic Ferromagnets)



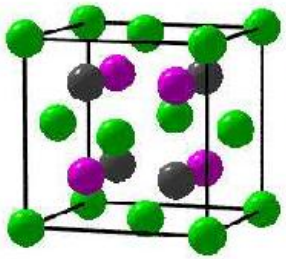
Half metals are ferromagnets whose density of states shows only one occupied spin-polarized sub-band at the Fermi energy E_F. Normal ferromagnets, like Fe and Co, have not only spin-polarized 3d electrons but also unpolarized 4s electrons at E_F. Half metals are compounds of more than one element and are mostly oxides or Heusler alloys.

Half Metallic Ferromagnets



R.A. de Groot et al., PRL 50, 2024 (1983)

The concept of half metallic ferromagnets was introduced by de Groot et al. on the basis of band structure calculations in NiMnSb and PtMnSb semi-Heusler phases.



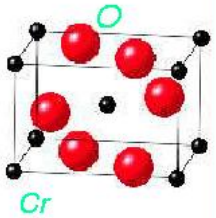
Ni
Mn
Sb

$C1_b$- structure (F43m space group)

Obvious conditions for the occurrence of this new class of materials are the existence of narrow bands and energy gaps in the energy spectrum, and strong ferromagnetic interactions.

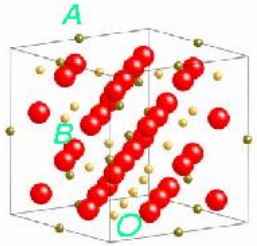
Existing half-metallic magnets

CrO_2



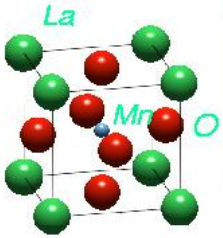
Chromium dioxide is the only simple oxide that is a ferromagnetic metal. Its resistivity increases rapidly as the temperature approaches the Curie point (T_C=398K)

Fe_3O_4



The oldest magnetic material known to man, Fe_3O_4 is also the half-metal with the highest Curie temperature of 860K.

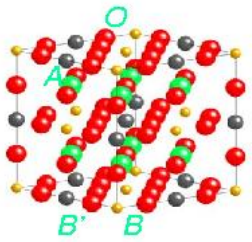
Mixed Valence Manganites



T_C of mixed-valence manganites cannot be increased above 400K.

$La_{(1-x)}A_xMnO_3$, A=Ca, Ba, Sr, x~0.3

Double Perovskites



Double Perovskites such as Sr_2FeMoO_6 and Sr_2FeReO_6 are claimed to be half metals with T_C higher than 400K.

$A_2BB'O_6$, A=Ca, Sr, Ba
B – 3d transition metal (Fe, Co)
B' – 4d transition metal (Mo, Re)

•Heusler and half-Heusler compounds (e.g. NiMnSb)

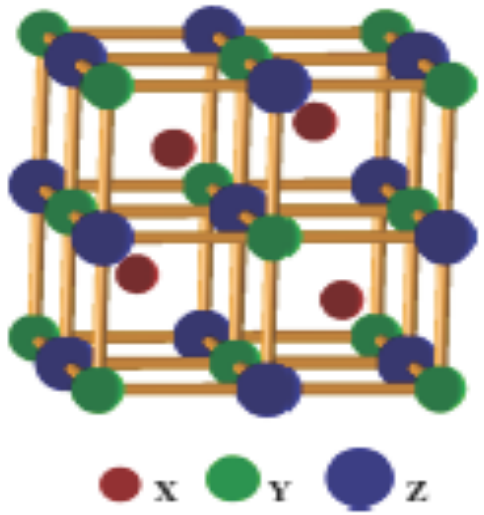
Direct observation of half-metalicity in Co2MnSi , Nature Comm. 2014

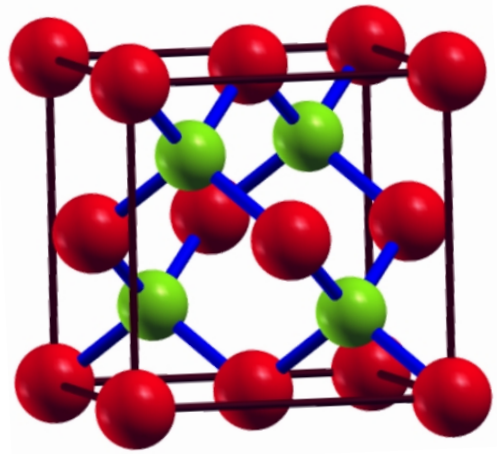
Half-Heusler Compounds (XMZ)

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

22	23	24	25	26	27	28	50	51
Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Sn**	**Sb**
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

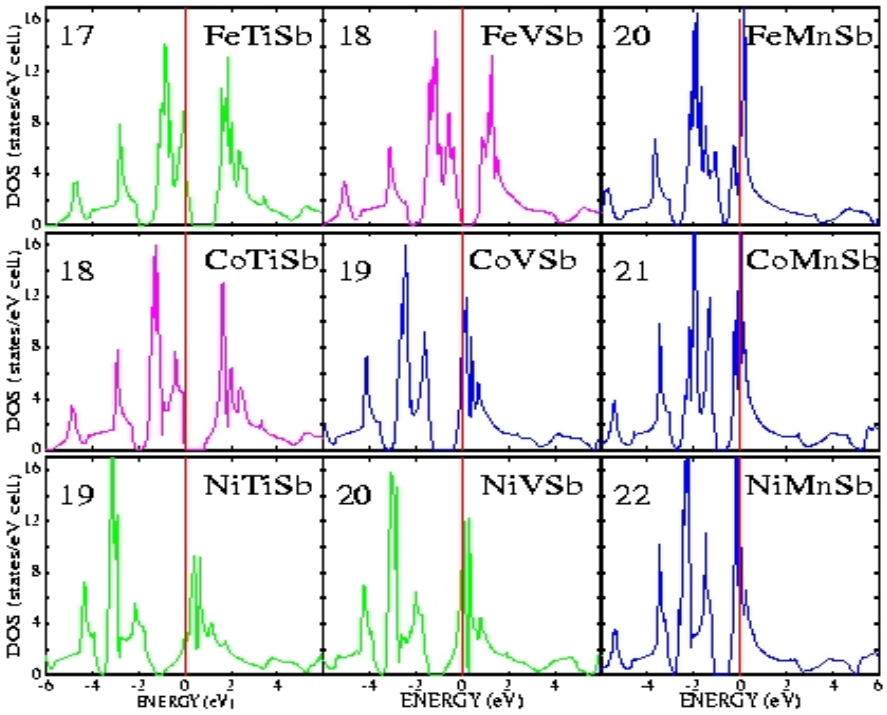
← M → ← X → Z





- The Zinc Blende structure adopted by semiconductors like GaAs, ZnSe, InAs. X = Ga, M = Empty, Z = As.
- 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.**

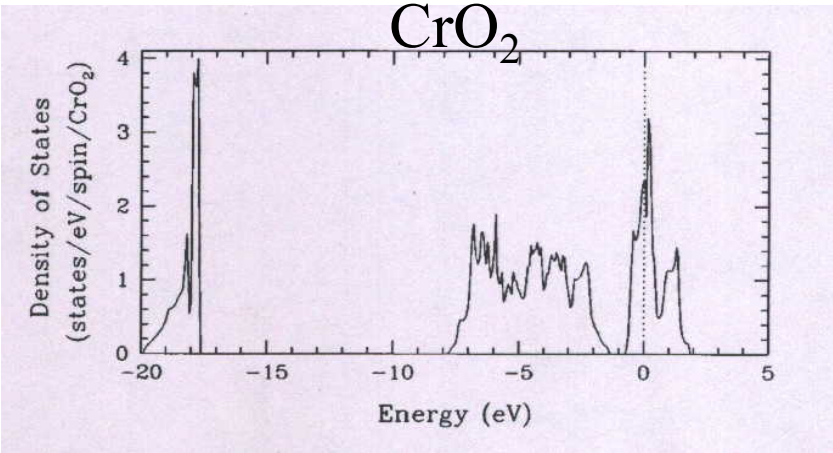
VEC = 18 Compounds are semiconductors.

VEC > 18 Compounds may be half-metallic ferromagnets.

Is gap a generic feature in half-metallic magnets ?

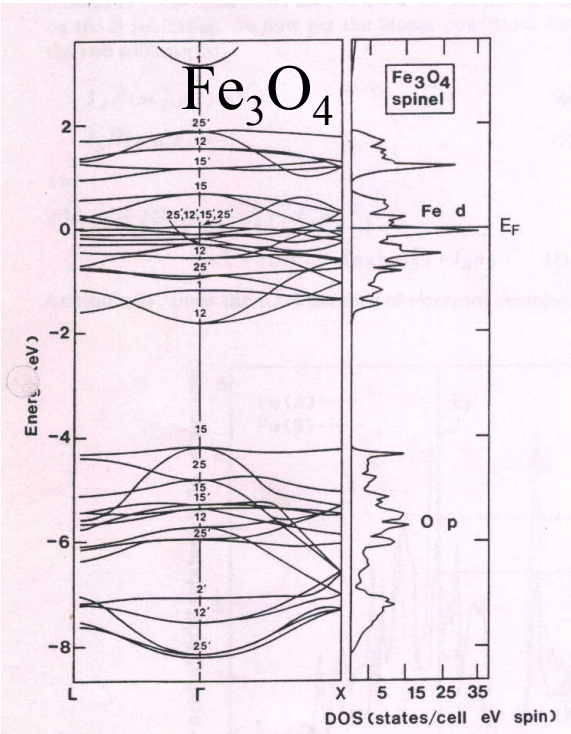
Spin integrated DOS of other half-metallic magnets

CrO_2



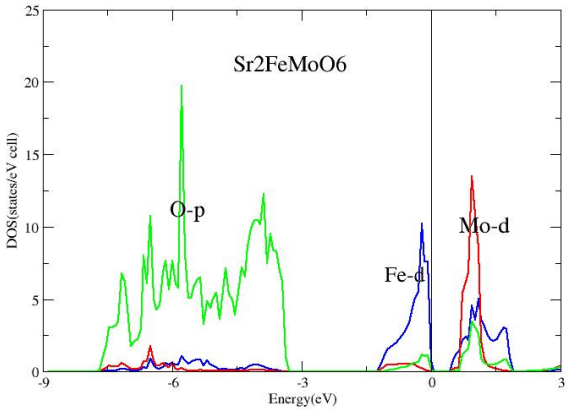
Lewis et.al. PRB 55 10253 (1997)

Fe_3O_4



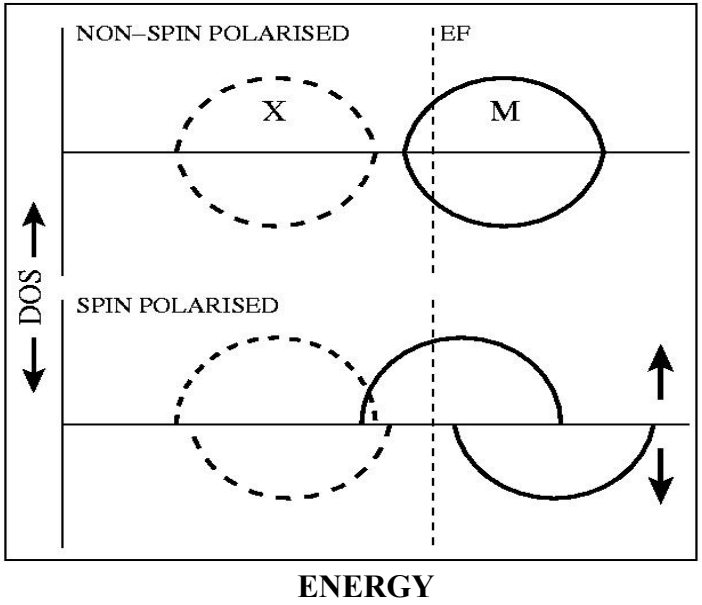
Zhang and Satpathy,
PRB 44 13319 (1991)

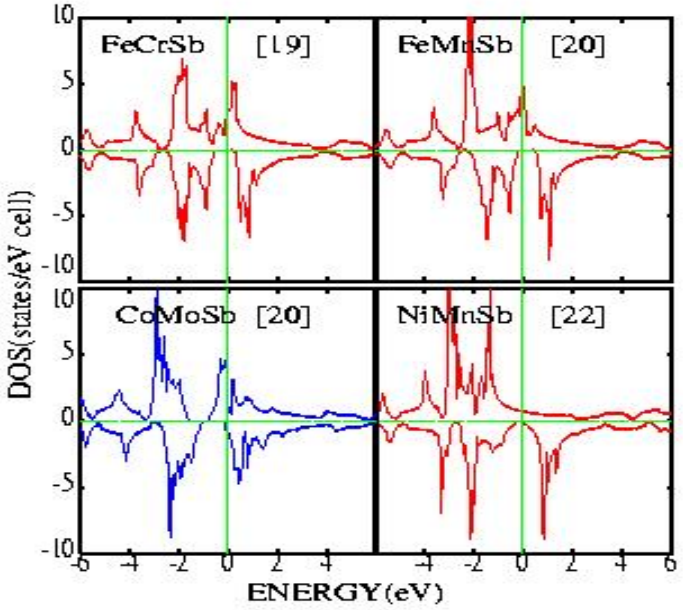
Sr_2FeMoO_6



Gap close to the Fermi level in the spin-integrated state is a generic feature for all existing half-metallic magnets.

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 semiconductors.**

Are doped half-Heusler compounds magnetic ?

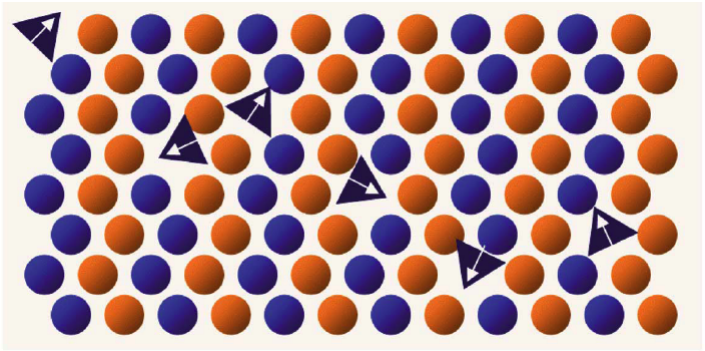
Diluted Magnetic Semiconductors

Semiconducting Material ↔Ferromagnetic Material

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

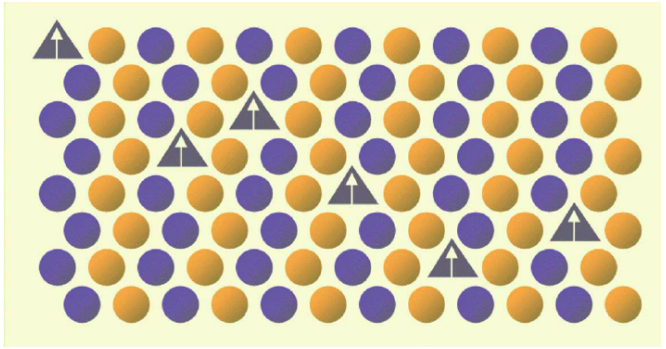
Carrier-mediated ferromagnetism

II-VI DMS (MnZnSe)

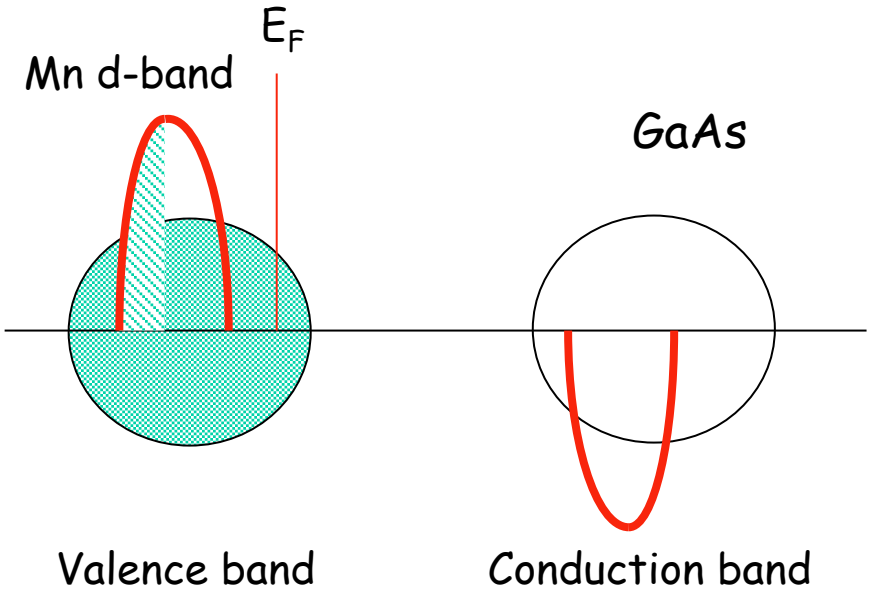


No carriers, no FM

III-V DMS (MnGaAs)



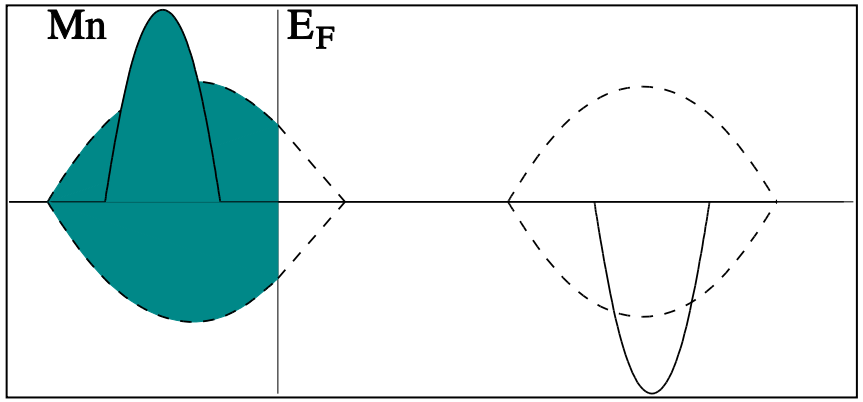
Mn = local moments +holes
Mn3+ →Mn2+ + holes →act as source of localized spins 5/2 +effective mass acceptors

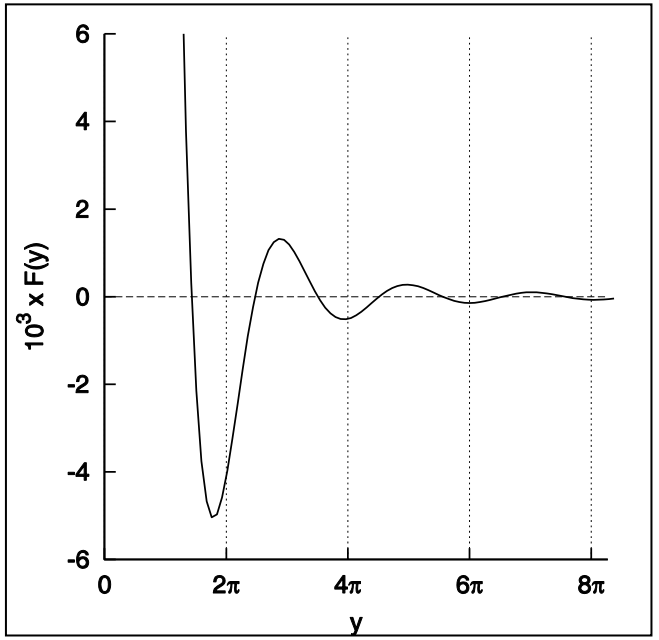


$$H = \int d^3 r J S(r).s(r)$$

$S(r)$ → Mn spin, $s(r)$ → hole spin

RKKY Model





The effective exchange interaction between the valence band hole and the spin J_{pd} results in a coupling between TM spins at a separation r given by

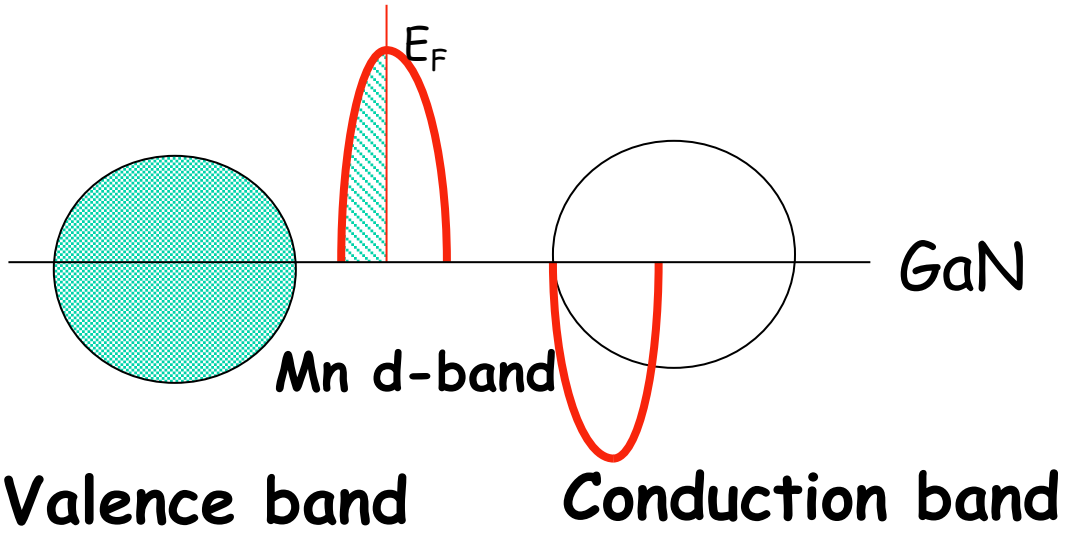
$$J(r) = Const \times J_{pd}^2 F(y)$$

$$F(y) = \frac{\sin y - y\cos y}{y^4}, \; y = 2k_F r$$

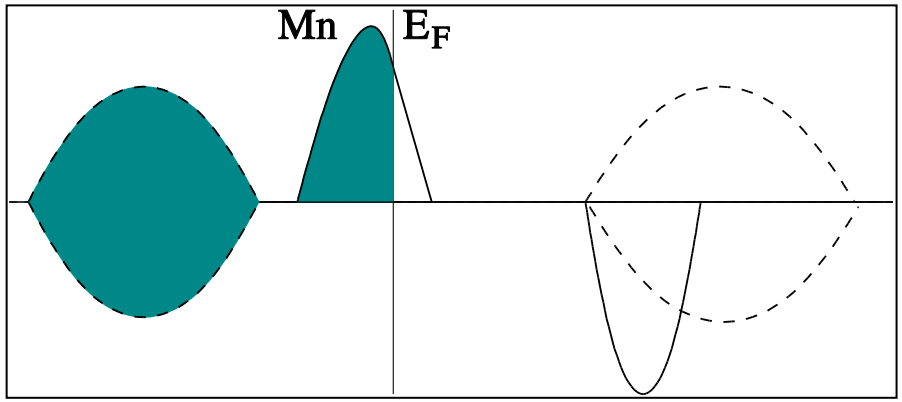
So materials with larger J_{pd} should have higher Tc

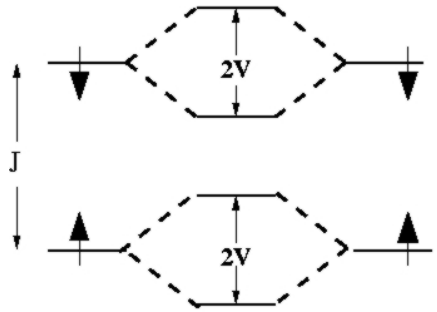
Schematics Mn doped GaN

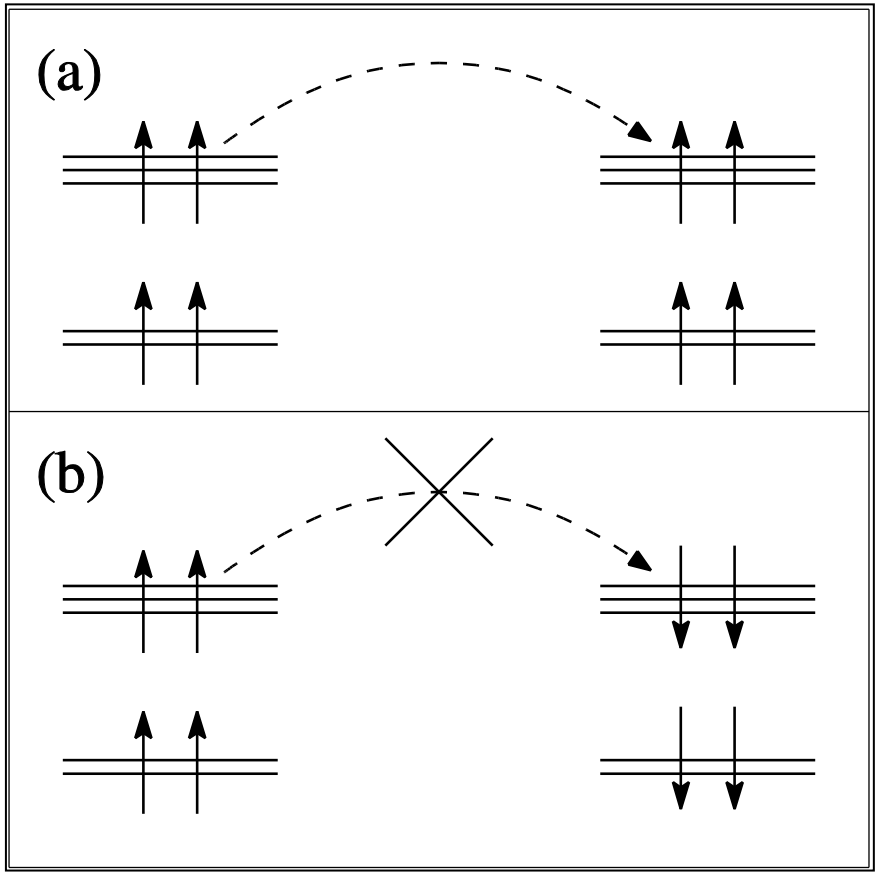
Impurity band forms in the gap, ferromagnetism is mediated by Double Exchange (Mn^{3+}) (d^4)



Double Exchange

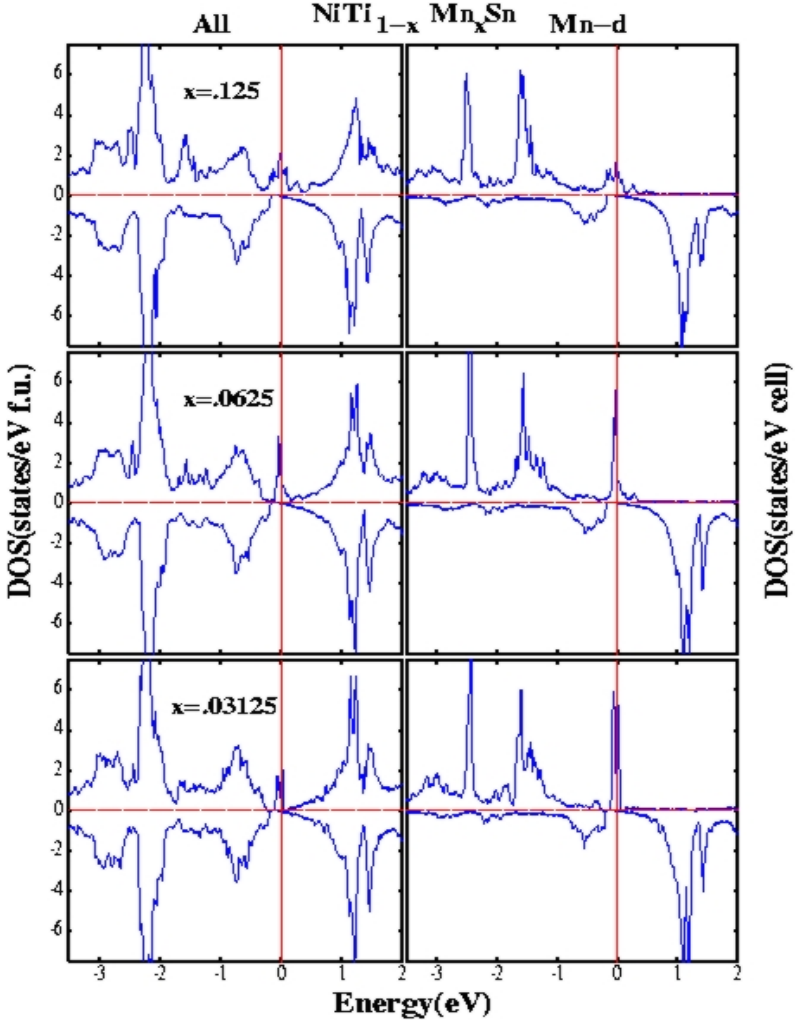


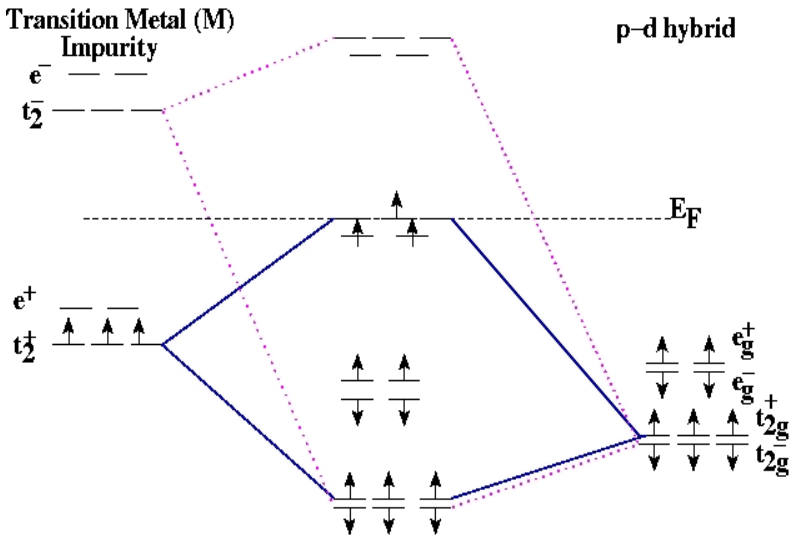




- **If the impurity band is partially occupied and the neighboring site has parallel spin (FM arrangement) then by the allowed hopping to the neighboring site it lowers the kinetic energy and FM is stable.**

Mn doped NiTiSn

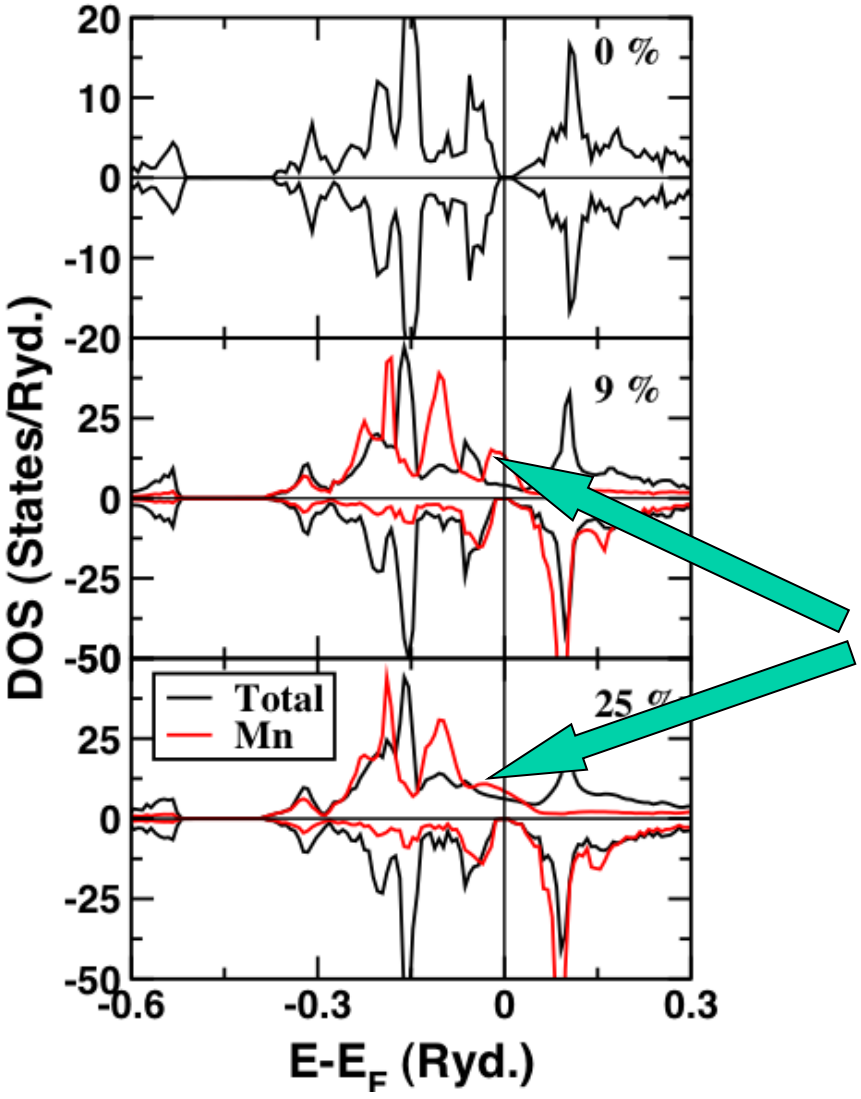




- **XYZ (VEC=18) ⇒ semiconducting.**
  Doped system ⇒ X(Y,Mn)Sb (VEC>18) half-metallic

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)

Mn Doped NiTiSn Disordered System (KKR-CPA Calculations)



(Ni-d)-(Ti-d) hybridization gap

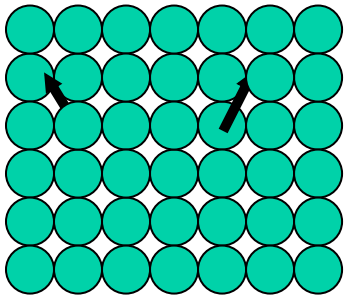
$(Mn_xTi_{1-x})NiSn$

Mn : 4^+, d^3 M=3 μ_B/cell

Mn impurity band at E_F

Classical Heisenberg Hamiltonian

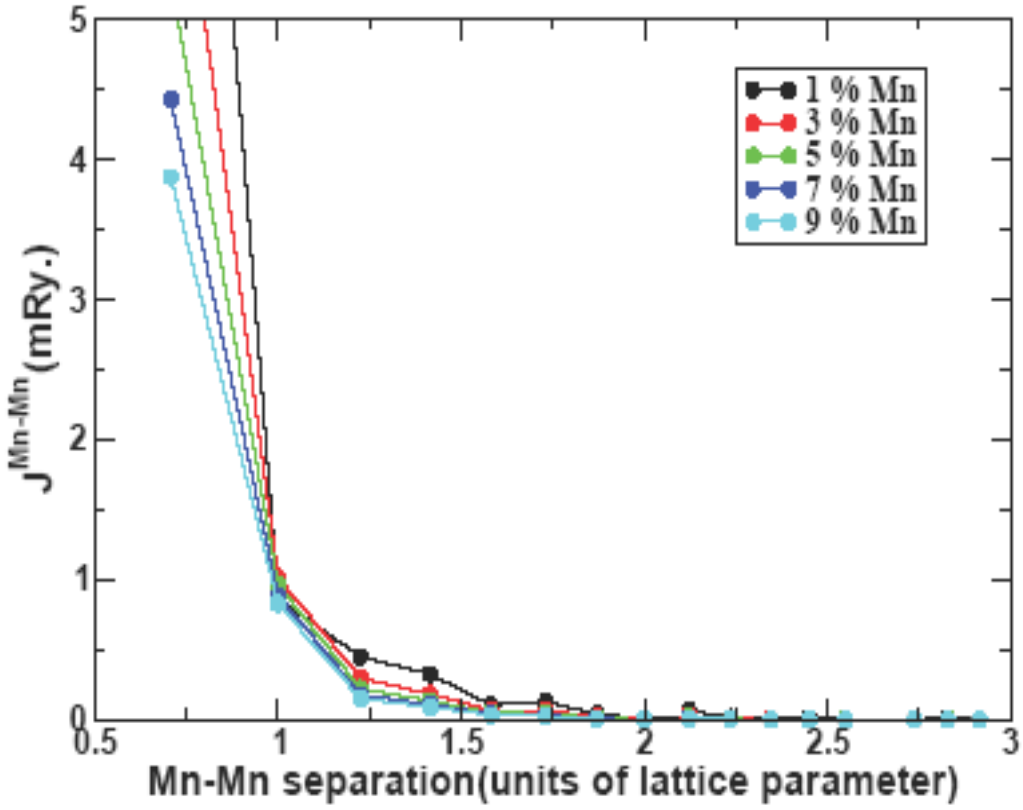
$$H = -\sum_{i \neq j} J_{ij} \vec{e}_i \vec{e}_j$$



From Microscopic to Atomistic

$$J_{ij} = \frac{1}{4\pi} \int^{E_F} dE \, \mathrm{Im}\{Tr_L(\Delta_i T_\uparrow^{ij} \Delta_j T_\downarrow^{ji})\} \qquad \Delta_i = t_{i\uparrow}^{-1} - t_{i\downarrow}^{-1}$$

Exchange interaction with disorder (CPA)

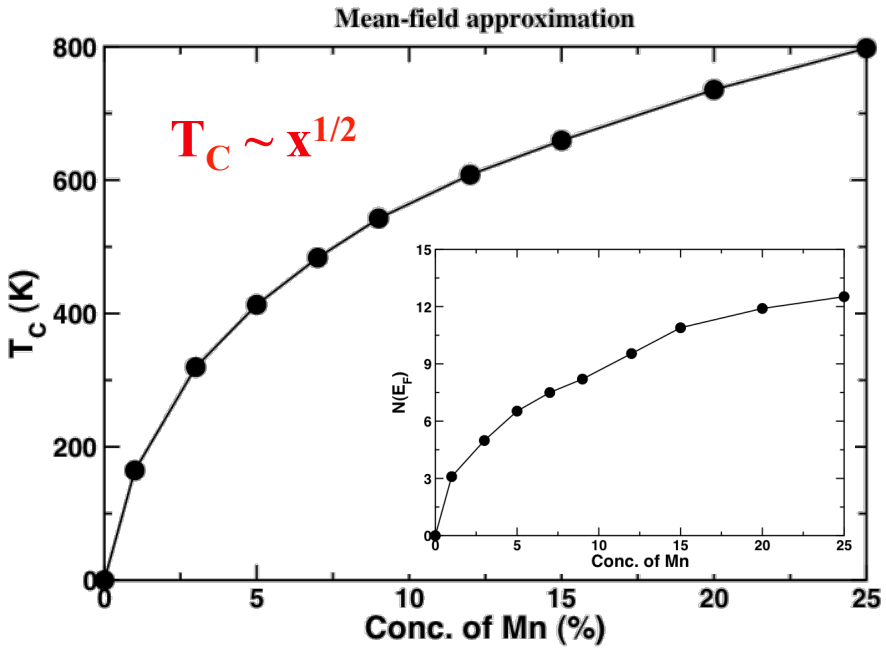


Short-ranged interaction

Exponential damping due to gap

Magnetic percolation

Mean field estimations



Short-ranged interaction

Exponential damping due to gap

Magnetic percolation

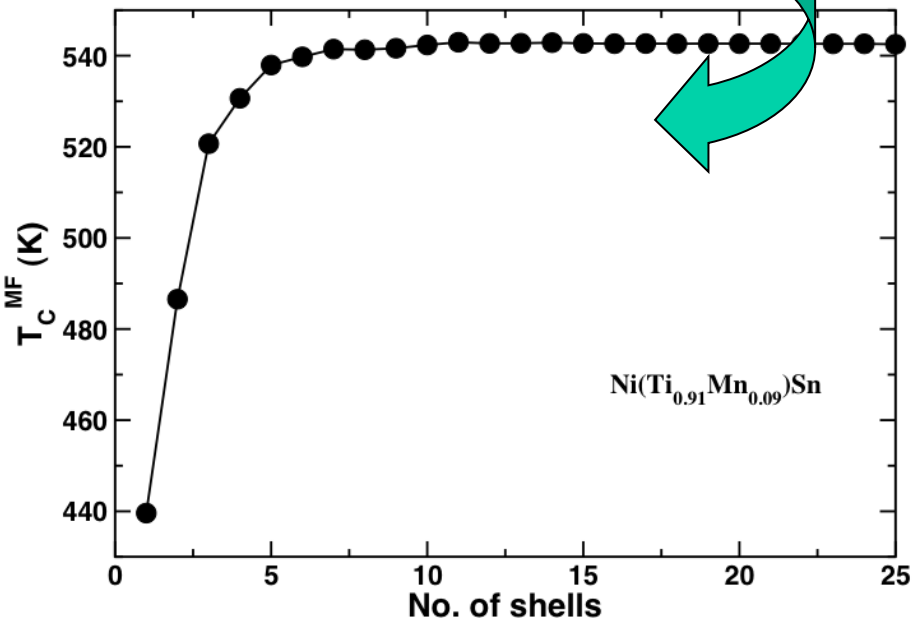
Double exchange : FM is favorable

TB model :-

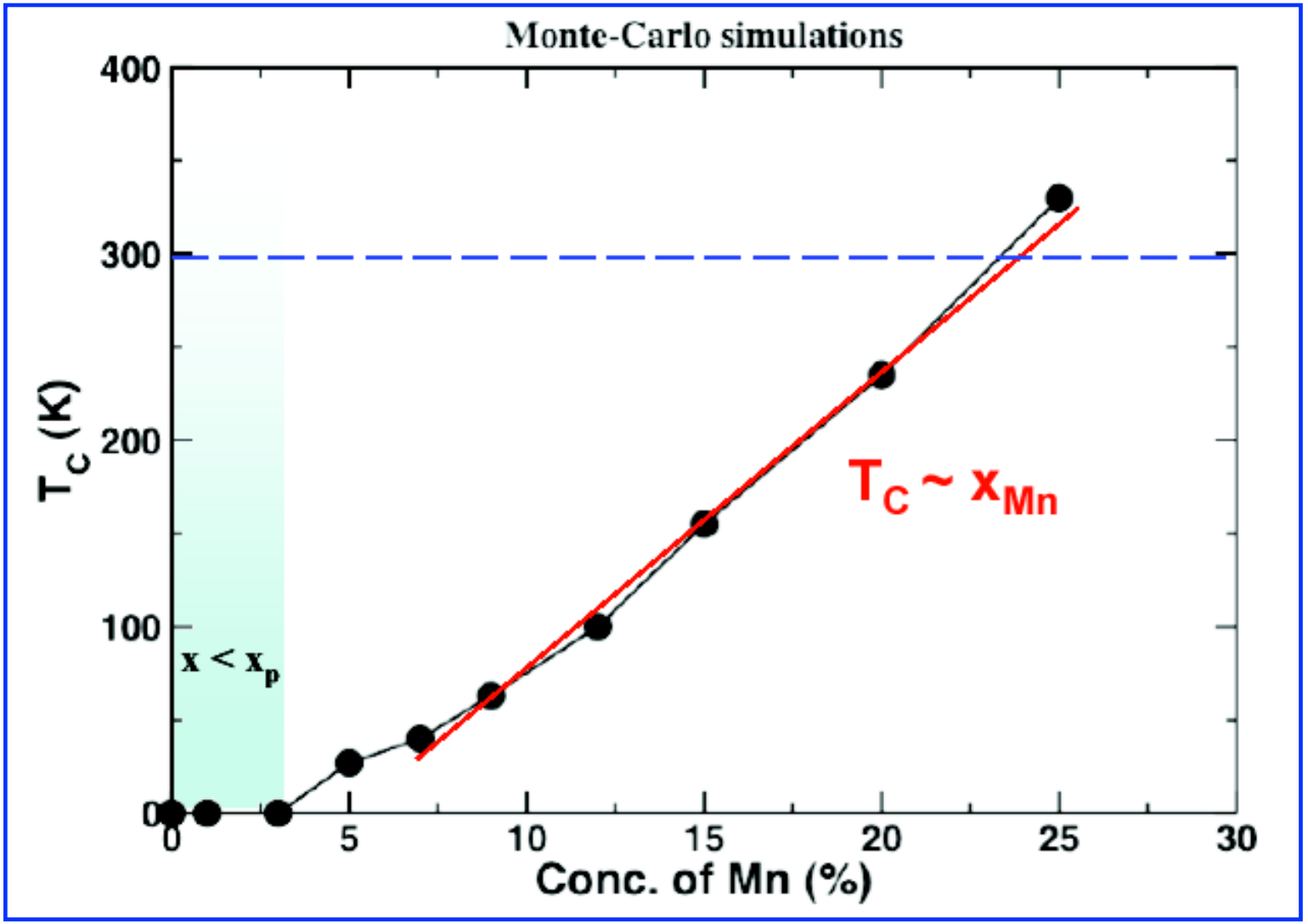
$$< W^2 >_{conf} = \sum_{j \neq 0} < | H_{0j} |^2 > = x \sum_{j \neq 0} | t_{0j} |^2$$

$$T_C^{MF} = \frac{2x}{3k_B} \sum_{j \neq 0} J_{0j}$$

x : Mn conc.

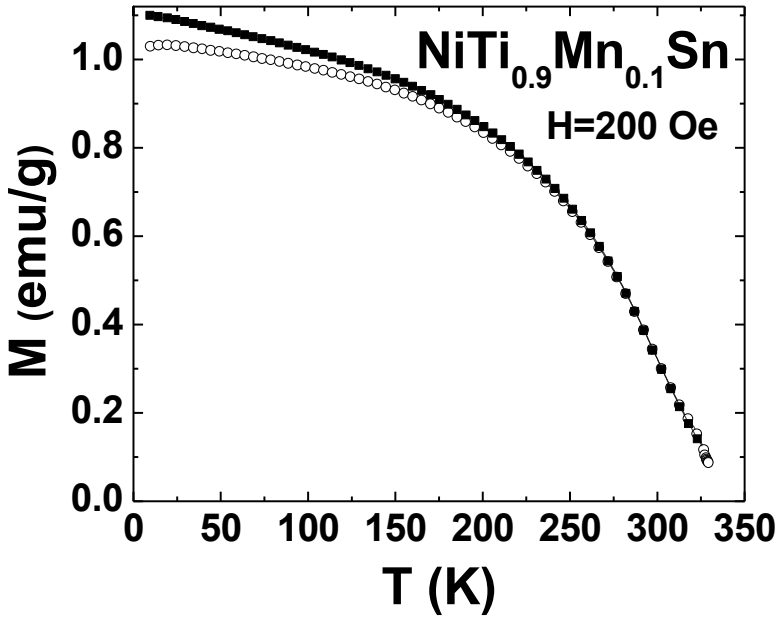


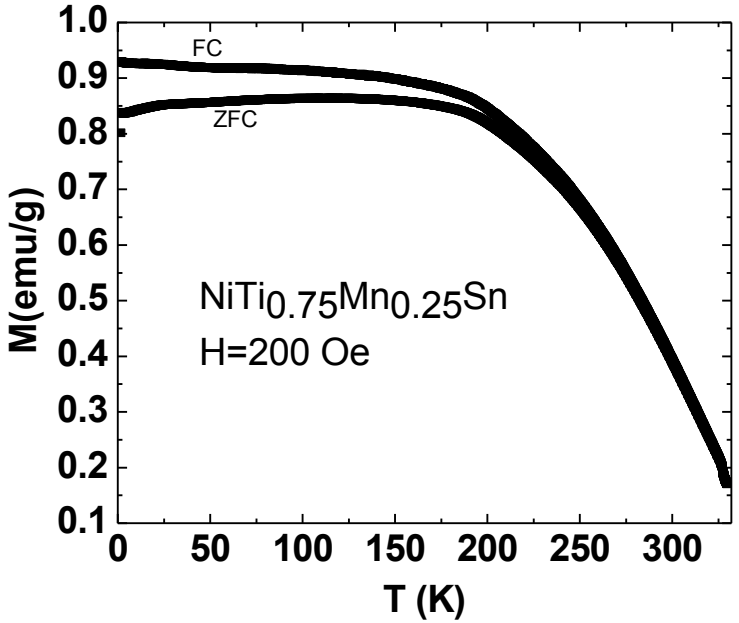
Monte- Carlo Simulations



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

Experimental Signature of ferromagnetism: Temperature dependence of magnetization of $NiTi_xMn_{1-x}Sn$

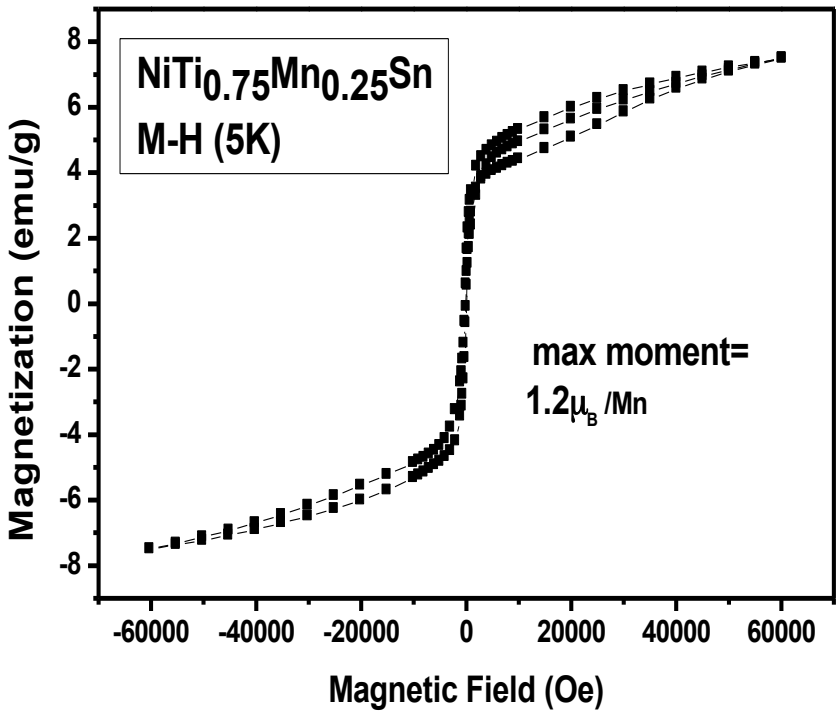


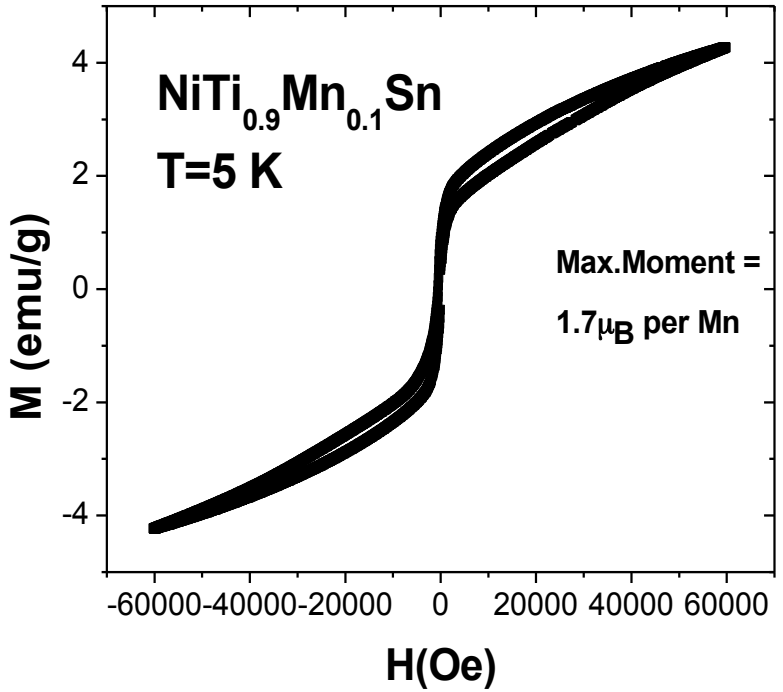


K. G. Suresh et al.

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

Experimental Signature of Ferromagnetism





M-H plots of $NiTi_{0.75}Mn_{0.25}Sn$ and $NiTi_{0.9}Mn_{0.1}Sn$

K. G. Suresh et al.

Mn doped Ge Clathrates: A Novel DMS System?

Nirmal Ganguli
Univ. of Twente,
The Netherlands

DST

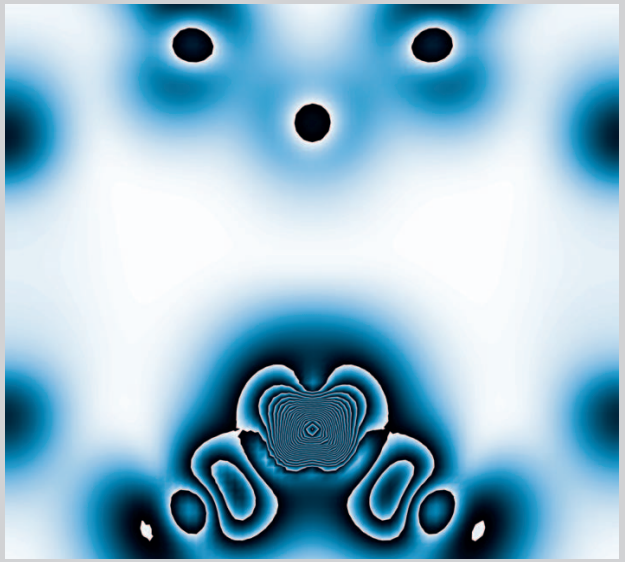
ISSN 0953-8984

Journal of Physics
Condensed Matter

Volume 24 Number 50 19 December 2012 505501

Featured in this issue
Liquids, Soft Matter and Biological Physics

Topical review
Kinetics of protein unfolding at interfaces
Yohko F Yano



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Germanium Clathrates

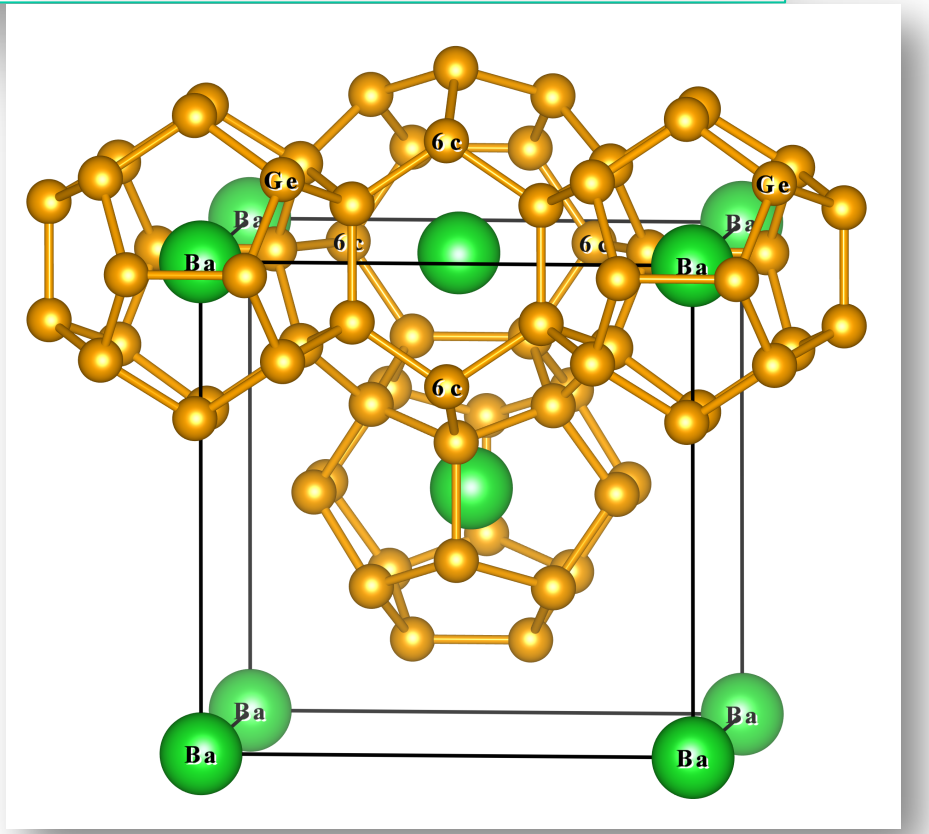
- Clathrate (Ge46) ≡ cage like structure

- Ge_{46} clathrate can be stabilized by incorporation of Ba

➢**Good thermoelectric material**

➢**Useful for hydrogen storage**

➢**Exhibits superconductivity**



Magnetism in Clathrates

nature Vol 443|21 September 2006|doi:10.1038/nature05145

LETTERS

A guest-free germanium clathrate

Arnold M. Guloy[1,2], Reiner Ramlau[1], Zhongjia Tang[1,2], Walter Schnelle[1], Michael Baitinger[1] & Yuri Grin[1]

Ba8Mn2Ge44 clathrate shows FM with 0.8 μB/Mn moment, Tc = 10K

APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 21 20 NOVEMBER 2000

Ferromagnetism in germanium clathrate: $Ba_8Mn_2Ge_{44}$

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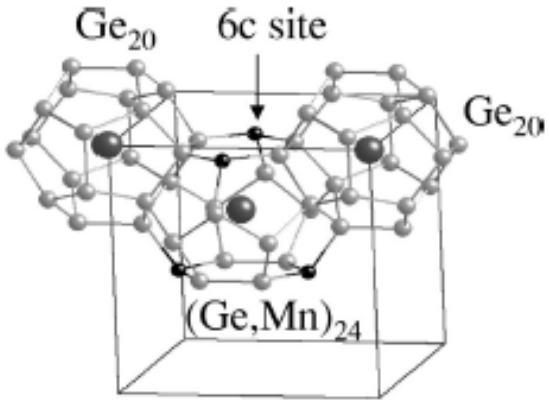
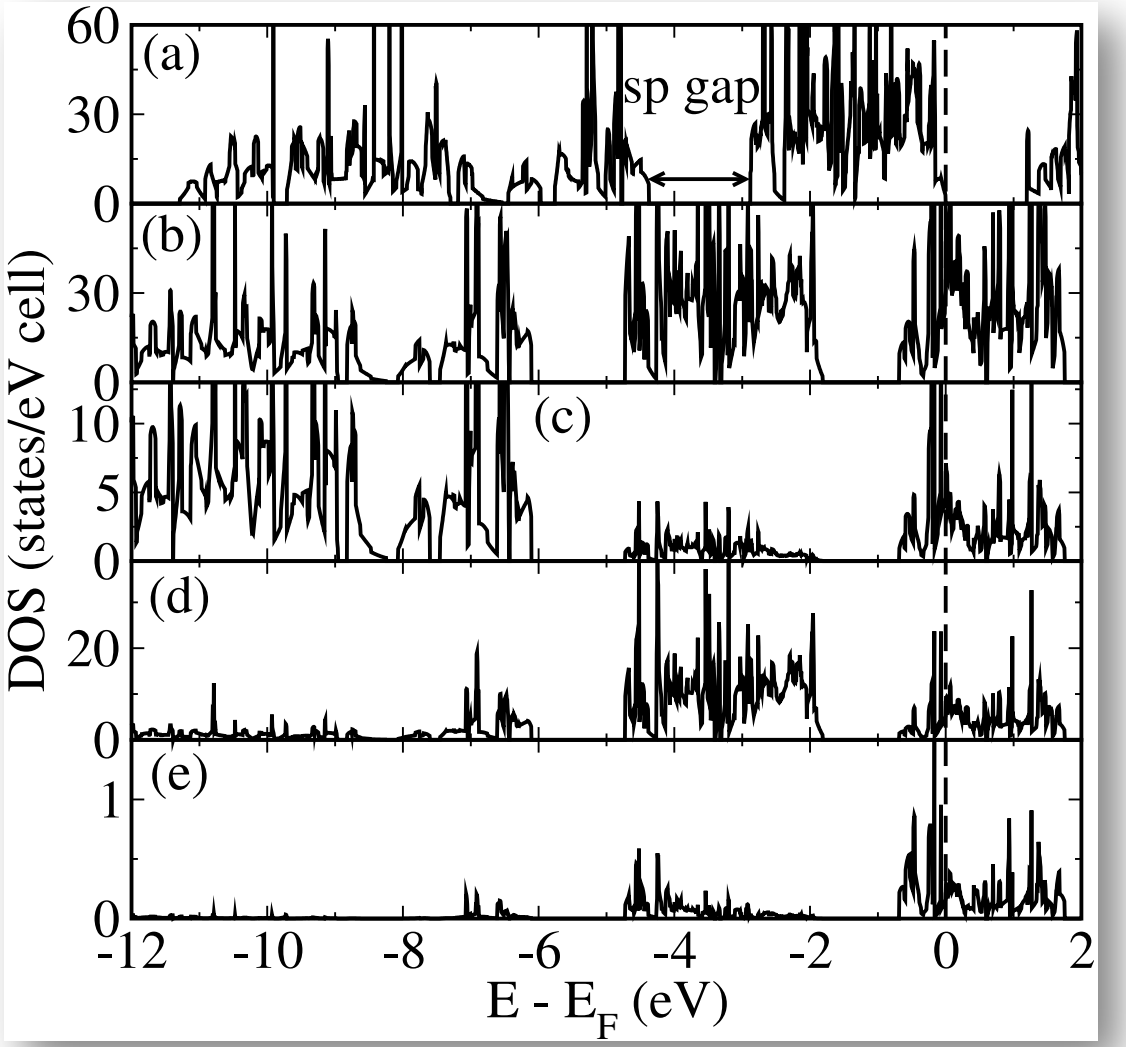
(Received 24 July 2000; accepted for publication 25 September 2000)

A unique magnetic nanosystem, constructed from Ge_{20} dodecahedrons and Mn, is presented, which shows a ferromagnetic transition around 10 K. In this system with the formula $Ba_8Mn_xGe_{46-x}$ ($x = 1-2$), the Mn atoms can be incorporated with accurate control in position of the crystal lattice. The spontaneous magnetization is approximately linearly proportional to the amount of Mn introduced and is maximized at $x = 2$. Magnetic measurements reveal that the *d* electrons are almost localized on Mn atoms but also affected by conduction electrons spreading over the clathrate network. [S0003-6951(00)04547-2]



Electronic Structure of Ge_{46} Clathrates



Ge_{46} 1.19eV

Ba_8Ge_{46}

Ge-s

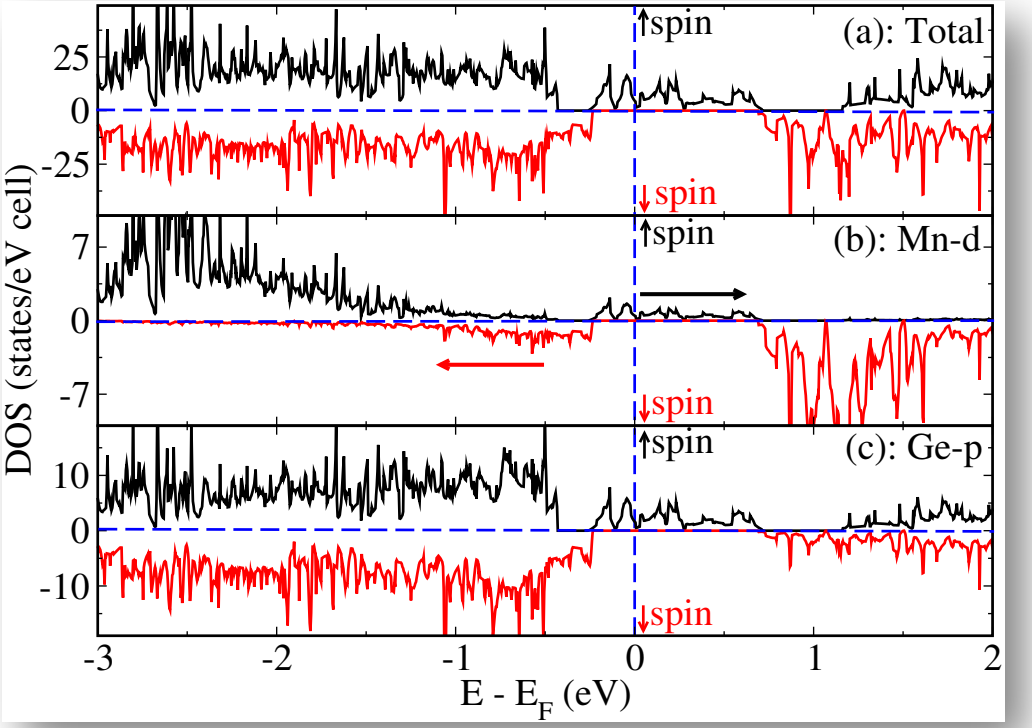
Ge-p

Ba-s

Doping Mn at 6c sites → Magnetic ?

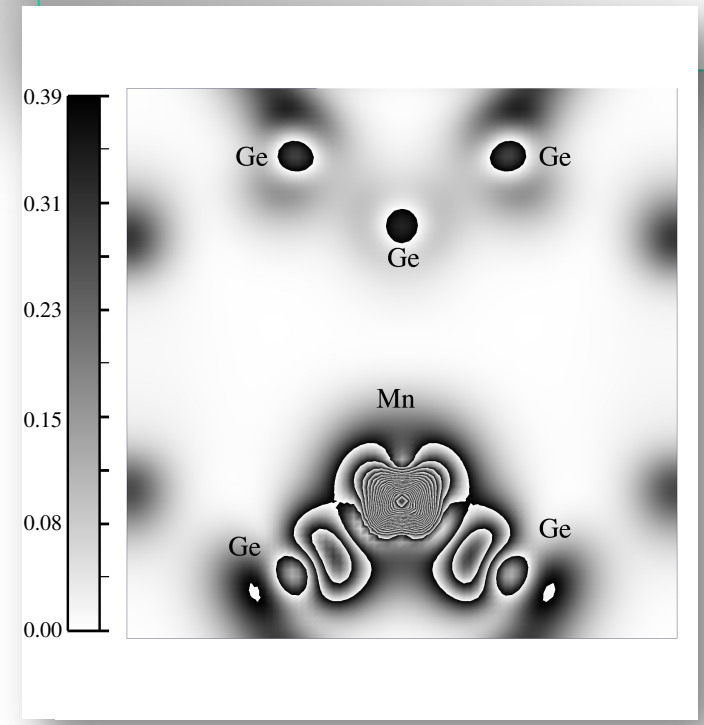
Mn doped Ge_{46} clathrate

- Ferromagnetic interaction between Mn atoms for both distances ($a/2$ and $\sqrt{6}a/4$), except vary high value of U



Hybridization induced –ve exchange splitting

Charge density

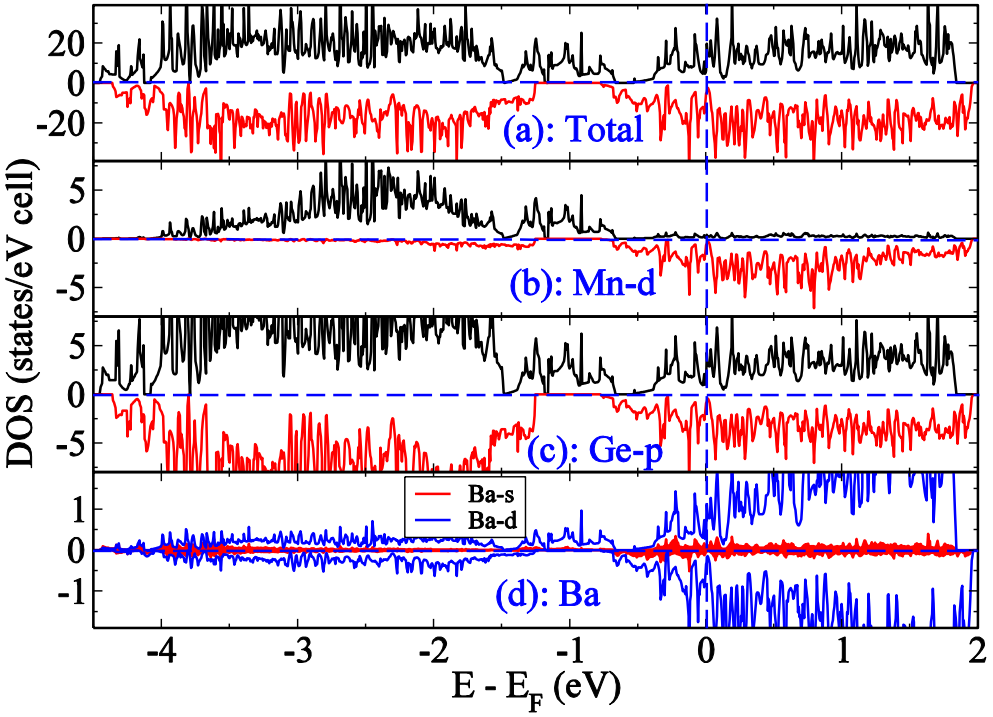


The charge density corresponding to valence band hole states

Exchange Interactions

U (eV)	Configuration I		Configuration II	
	$E_{AFM} - E_{FM}$ (meV)	magnetic moment (μ_B per cell)	$E_{AFM} - E_{FM}$ (meV)	magnetic moment (μ_B per cell)
0.0	186.3	6.0	151.1	6.0
2.0	182.5	6.0	145.2	6.0
4.0	171.6	6.0	134.3	6.0
5.0	21.5	7.6	14.4	7.7
6.0	10.3	8.2	5.2	8.2
7.0	-6.1	8.5	-8.5	8.7

Mn doped Ba_8Ge_{46}

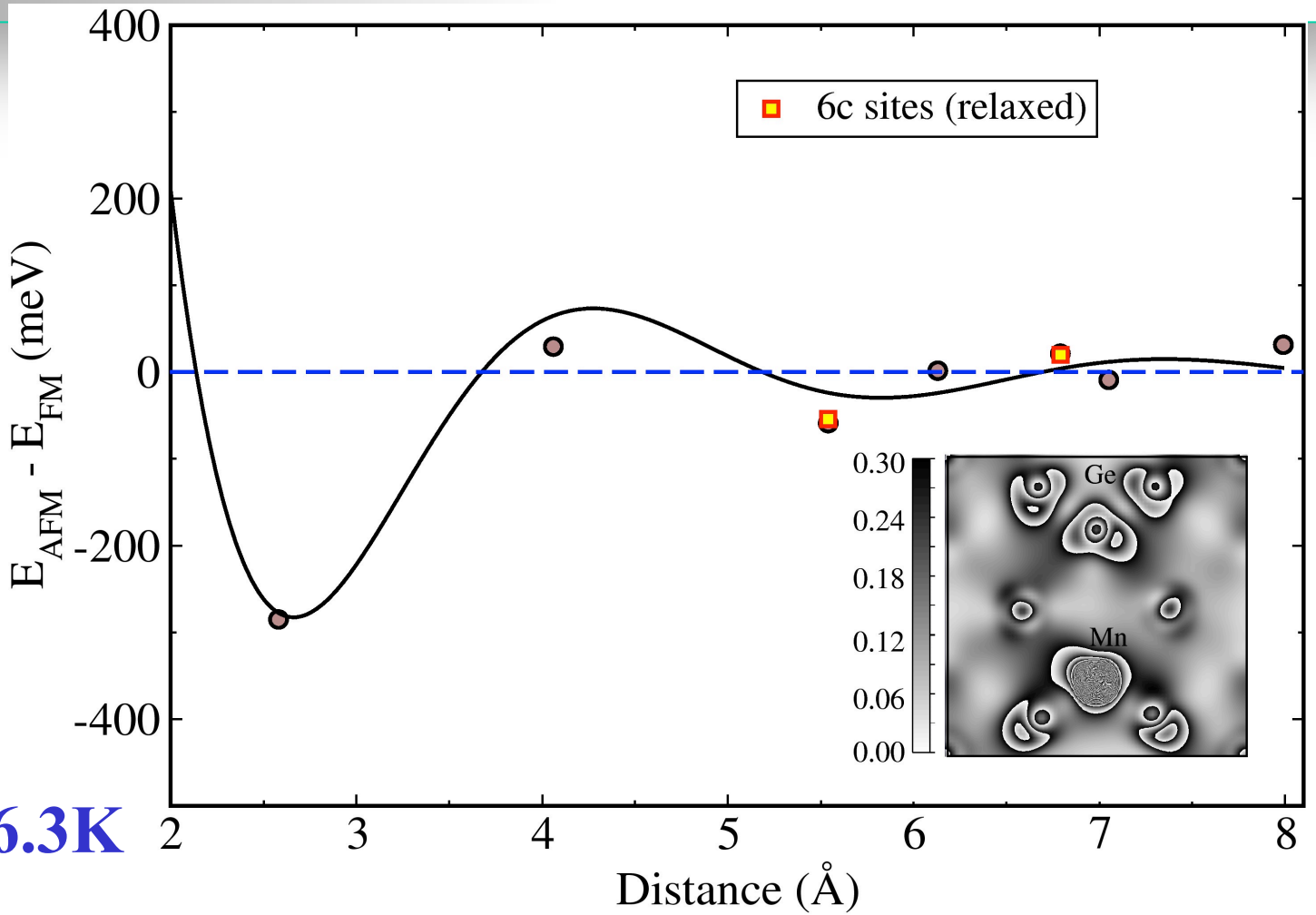


- DOS is metallic
- $E_x/E_f << 1$ → RKKY Limit
- E_x → Exchange splitting of the host band, E_f → Fermi level

Exchange Interactions

U (eV)	Configuration I		Configuration II	
	$E_{AFM} - E_{FM}$ (meV)	magnetic moment (μ_B per cell)	$E_{AFM} - E_{FM}$ (meV)	magnetic moment (μ_B per cell)
0.0	-22.8	6.1	22.7	6.1
4.0	-54.2	6.3	19.9	6.4
5.0	-56.4	7.5	12.2	7.6
7.0	-142.0	9.1	9.3	9.2

Mn doped Ba_8Ge_{46}



Tc = 6.3K

$$J(r) = \text{Constant} \times [\sin(2k_F r) - 2k_F r \cos(2k_F r)]/r^4$$

Clathrates: summary

- Ge_{46} clathrate has higher band gap than Ge in diamond structure
- Hybridization induced negative exchange interaction promotes ferromagnetism for Mn doped Ge_{46} clathrates
- Ba atoms at the center of the cages provide conduction electrons
- In the presence of conduction electrons, RKKY-like interaction is operative in Mn doped Ba_8Ge_{46} clathrates
- Experimental observations (low Curie temperature and low saturation magnetic moment) can be explained


Thank You