Theory for ferromagnetism in disordered systems.

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I- Introduction.

II- RPA for disordered magnetic systems.

III- Diluted Magnetic Semiconductors.

IV- Conclusions.

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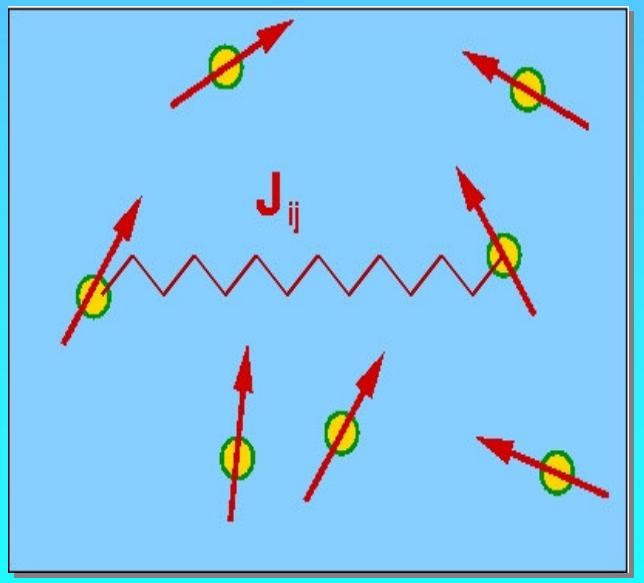
I- Introduction.

Aim: Study the magnetic properties of disordered magnetic systems ***(Curie temperature, magnetic excitations spectrum, local moments, ...)*** *of a system of* N_{imp} *interacting magnetic impurities with spin* S *(quantum or classical) randomly distributed on a given lattice.*

$$H = -\sum_{ij} p_i \, p_j \, J_{ij} \, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

$$(p_i = 1 \text{ if the site is occupied otherwise } 0)$$



The approach should be able to:

- *Treat disorder effects beyond a simple Virtual Crystal Approximation (VCA).*
- *Treat properly thermal and quantum fluctuations beyond Mean Field (MFT).*

A-No disorder: treatment of thermal fluctuations.

Mean Field Theory for Heisenberg model:

$$H_{MF} = \sum_i h_i^{eff} S_i^z \quad avec \quad h_i^{eff} = \sum_j J_{ij} \left\langle S^z \right\rangle$$

$$\left\langle S^z \right\rangle = S B_S \left(\frac{h_i^{eff}}{k_B T} \right)$$

$$\Rightarrow \quad k_B T_C = \frac{1}{3} S(S+1) \sum_j J_{0j}$$

MFT has several shortcomings.

- *Underestimate the effects of thermal fluctuations.*
- *Collective excitations are not included.*
- *Violate both theorems, Mermin-Wagner and Goldstone (finite Curie temperature for 1D et 2D)*

B- How to improve the treatment of thermal and transverse fluctuations?

RPA (Random Phase Approximation) *(details of the derivation will be given for the general case of disordered systems.)*

✓ *Includes collective excitations.*

✓ *Fulfils both theorems Mermin-Wagner and Goldstone (in absence of anisotropy T_C=0 for1D and 2D)*

$$k_B T_C^{RPA} = \frac{1}{3} S(S+1) \frac{1}{\frac{1}{N}\sum_q \frac{1}{\omega(q)}} \quad , \; \omega(\mathrm{q}) = J(0) - J(q)$$

✓ *Better treatment of thermal fluctuations.*

✓ *Very good agreement with* **exact** *Monte Carlo (*Peczack et al. PRB 1991, Chen et al. PRB 1993*) calculations.*

simple cubic lattice, nearest neighbor exchange J.

$$k_B T_C^{MC} = 1.44\, J, \quad k_B T_C^{RPA} = 1.39 J, \quad k_B T_C^{MF} = 2J$$

II- RPA for disordered systems.

- *Virtual Crystal Approximation (VCA) over simplified to treat the disorder effects:* $T_C(x) = x\, T_C(1)$
- *Monte Carlo calculations are too heavy et very costly in CPU, especially when the exchange couplings are long-ranged.*
- *RPA-CPA (Coherent Potential Approximation) (G.B and P. Bruno PRB 2002): does not allow to include the cluster effects and correlations in the disorder.*

Generalization of RPA by treating disorder effects exactly!!

[1] G. B. T. Ziman and J. Kudrnovsky, Europhys. Lett., **69** 812 (2005).
[2] G. B. T. Ziman and J. Kudrnovsky, APL **85**, 4941 (2004).
[3] G. B. T. Ziman and J. Kudrnovsky PRB **72**, 125207 (2005)
[4] R. Bouzerar, G.B. and T. Ziman , Phys. Rev. B **73**, 024411 (2006)
[5] G.B., R. Bouzerar,T. Ziman and J. Kudrnovsky, submitted (2005)
[3] G. B. and T. Ziman submited to Phys. Rev. (2006)

Summary of the theory.

*The approach is based on **real space** and **finite temperature** Green's functions formalism.*

$$G_{ij}(\omega) = \langle\langle S_i^+ ; S_j^- \rangle\rangle = -i\int_0^{+\infty} \left\langle \left[S_i^+(t); S_j^-(0) \right] \right\rangle e^{i\omega t} dt$$

- *Equation of motion for the retarded Green 's function.*

$$\omega G_{ij}(\omega) = 2\delta_{ij}\left\langle S_i^z \right\rangle + \langle\langle \left[S_i^+, H \right]; S_j^- \rangle\rangle$$

- *RPA decoupling of the higher order GF.*

$$\left(\omega - 2\sum_l J_{il} \left\langle S_l^z \right\rangle \right) G_{ij}(\omega) = 2\left\langle S_i^z \right\rangle \left(\delta_{ij} - \sum_l J_{il} G_{lj}(\omega) \right)$$

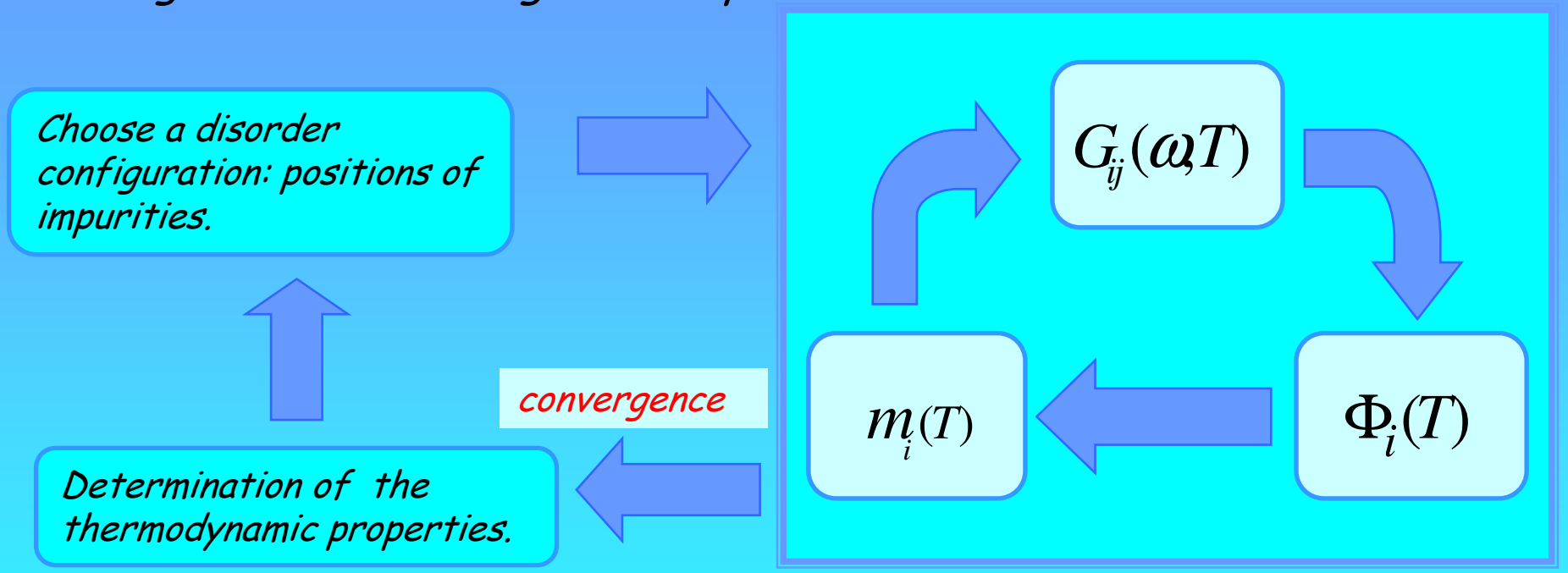
- *Equations for the local magnetizations to close the system (Callen).*

$$\left\langle S_i^z \right\rangle = \frac{(S - \Phi_i)(1+\Phi_i)^{2S+1} + (S+1+\Phi_i)\Phi_i^{2S+1}}{(1+\Phi_i)^{2S+1} - \Phi_i^{2S+1}}$$

$$with\ \Phi_i = -\frac{1}{2\pi \left\langle S_i^z \right\rangle} \int_{-\infty}^{+\infty} \frac{\Im \mathrm{m}\left[G_{ii}(\omega) \right]}{\exp(\beta\omega) - 1} d\omega$$

Local magnetizations and thermodynamic properties.

Summary of the procedure to determine the local magnetizations at a given temperature T.



For a given temperature T, after convergence one can calculate:

- *The distribution of the local magnetizations* $m_i(T)$.
- *The spectral function* $A(q,\omega,T)$ *and magnetic excitations.*
- *The spin-spin correlation functions* $\langle S_i . S_j \rangle$.
- *Etc. ……*

Semi-analytical expression of the Curie temperature

By combining together the previous set of equations one can derive a semi-analytical expression for the Curie temperature for disordered ferromagnetic systems.

$$k_B T_C = \frac{1}{3N_{imp}} S(S+1) \sum_i \frac{1}{F_i}$$

$$F_i = -\frac{1}{2\pi\lambda_i} \int_{-\infty}^{+\infty} \frac{\Im \mathrm{m}(G_{ii}(E))}{E} dE,$$

$$\lambda_i = \lim_{T \to T_C} \frac{\langle S_i^z \rangle}{m} \quad \left(m = \frac{1}{N_{imp}} \sum_{i=1}^{N_{imp}} \langle S_i^z \rangle \right)$$

Remark:

For the determination of the Curie temperature we explicitly use the fact that in the limit $T \to T_c$; $m_i \to 0$ but $\lambda_i \neq 0$ which are determined self-consistently!

This expression is the generalization of RPA to disordered ferromagnetic systems!

III- Diluted Magnetic semiconductors.

The strong interest for diluted magnetic is partly motivated by their technological potential in the domain of Spintronics.

⇒ Need for materials with relatively high Curie temperature (beyond room temperature).

⇒ Understand *experimentally* and *theoretically* which physical quantities control T_C :

- *Role and effects of disorder?*
- *Importance of thermal fluctuations?*
- *Influence of the band structure of the material?*
- *Dependence with the carrier density and magnetic impurities concentration?*
- *Effects of intrinsic defects (compensation)?*
- *…*

III-V Semiconductors: GaMnAs and GaMnN

A- Introduction.

1- GaMnAs is one of the most studied material and exhibits relatively high T_C : x_{Mn}=5% , T_C=110 K and x_{Mn}=7.5% , T_C=175 K.

2- GaMnN is more controversial: some pretends to observe paramagnetism and other ferromagnetism with very high Curie temperature.

- *In III-V materials the substitution of Ga^{3+} by Mn^{2+} introduce **simultaneously** a localized spin **S=5/2** and an itinerant carrier (hole) in the valence band or impurity band.*

- *The exchange between impurities is of « generalized RKKY-type » (polarization of the gas of carrier + effects of resonances).*

B- Compensation.

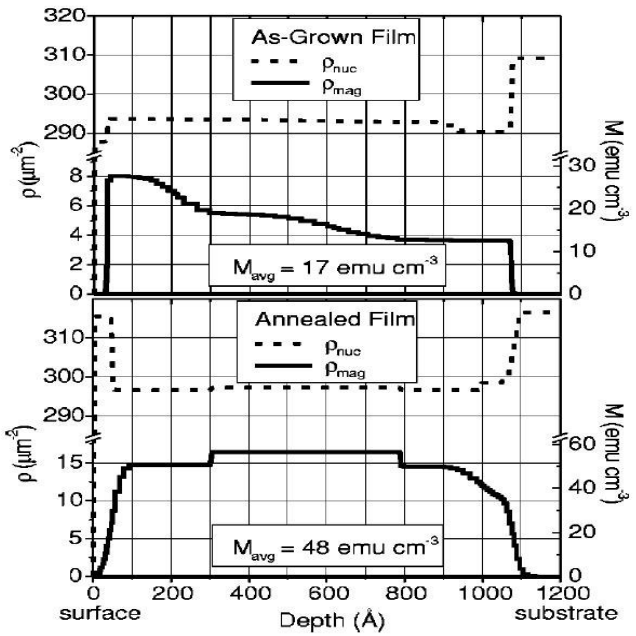
Additional source of disorder.

These defects appear during the MBE growth of the samples for example. These intrinsic defects have a drastic effects on both TRANSPORT and MAGNETISM.

There are two types of such defects:

- ✓ *As anti-sites which affect **only** the density of carrier.*
- ✓ *Mn(I) affect **both** the hole density and the density of magnetically active Mn.*

Profile of magnetization and density of Mn



Kirby et al. PRB (2004)

***Question**: Can we explain **quantitatively** the Curie temperatures measured experimentally?*

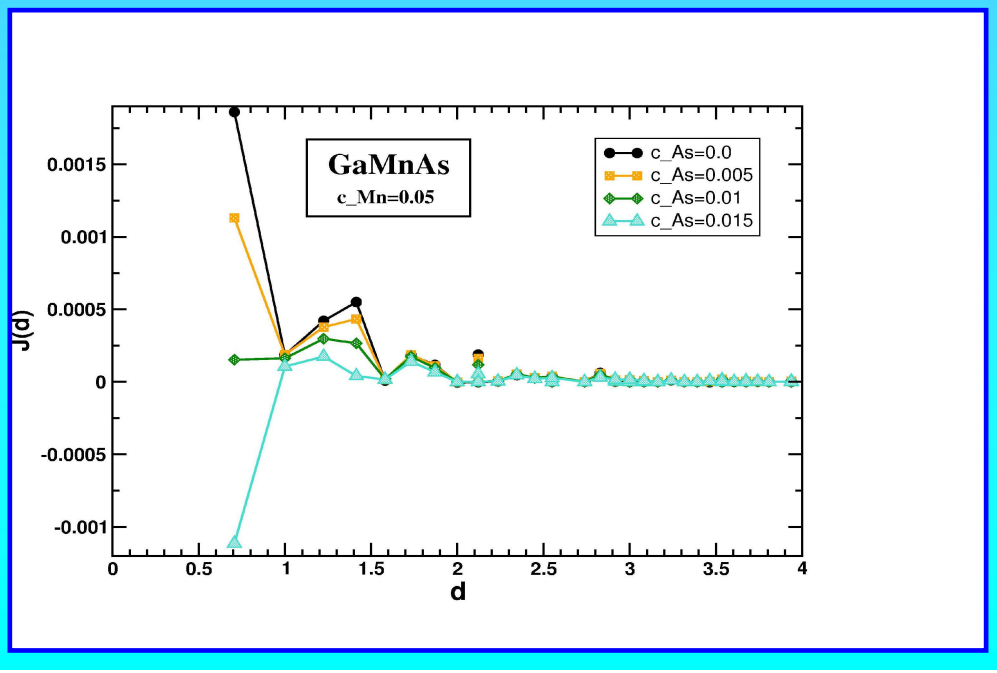
To allow a direct quantitative comparison, we choose an approach with **no adjustable parameters**.

A two step approach:

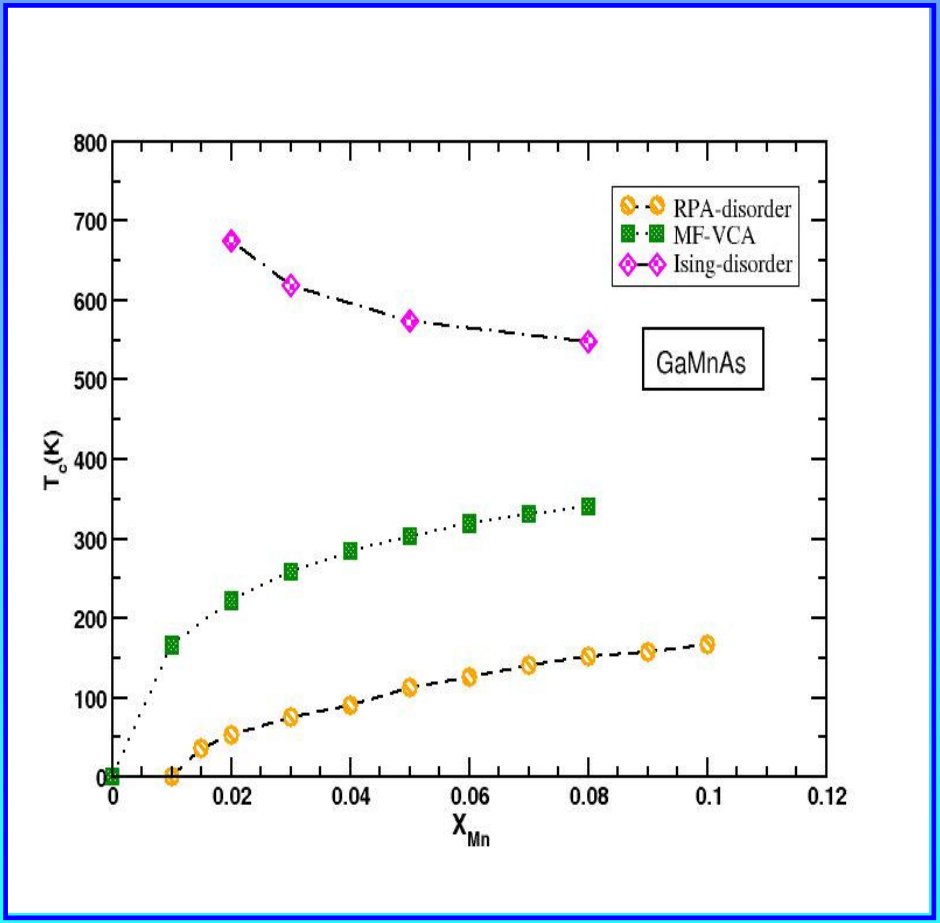
1- Determination of the exchange integrals J_{ij} from first principle methods (Tight Binding -Linear Muffin Tin Orbitals)

2- Proper treatment of the effective Heisenberg Hamiltonian to calculate the magnetic properties.

Couplings obtained within LDA calculations for GaMnAs in presence of As anti-sites.



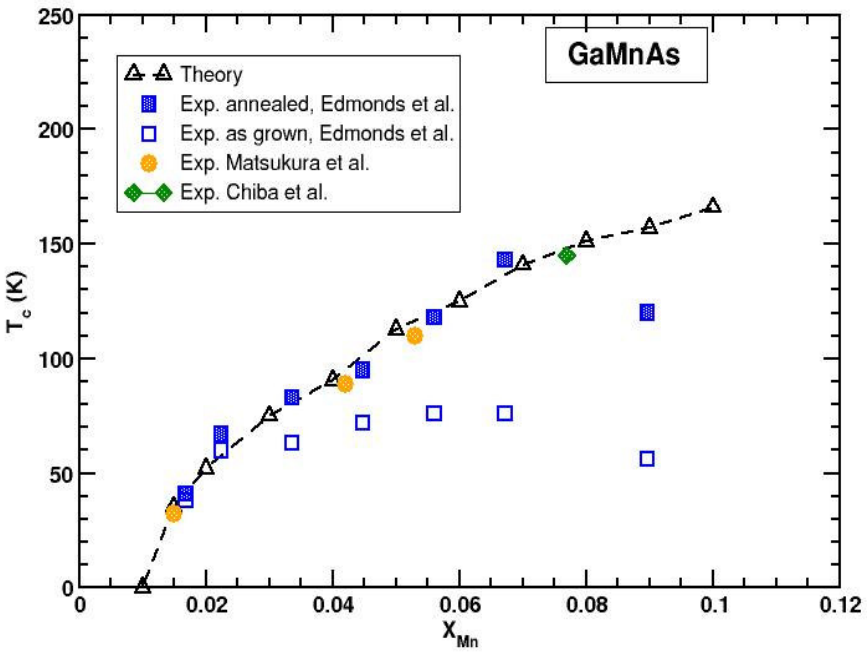
1- Different treatment of the Heisenberg Hamiltonian.



- *The Mean field VCA underestimates the fluctuations, and overestimates strongly the Curie temperature (for 5% Mn T_C=300 K).*
- *The «Ising» calculations: Effects of disorder included but not transverse fluctuations lead to non unrealistic values for T_C.*
- *The SC-LRPA lead to much smaller values for the Curie temperature.*
- *Good agreement with Monte Carlo: for 5% Mn and the same couplings : 137 K [1] et 103 K [2].*

[1] L. Bergqvist et al. Phys. Rev. Lett., **93** 137202 (2004)
[2] K. Sato et al. Phys. Rev. B, **70** 201202 (2004)

2- Comparison between experiment and theory for GaMnAs.



✓ *We observe a very good agreement between experiment and theory for optimally annealed samples (calculations are done for non compensated systems).*

✓ *« As-grown » samples exhibit much smaller Curie temperature: strong reduction due to the presence of compensating defects.*

✓ *The calculations provide the maximum value of the Curie temperature for each concentration of Mn.*

✓ *Below 1% no ferromagnetism (percolation threshold).*

Remark: (1) The TB-LMTO calculations to estimate the couplings and (2) the treatment of disorder and fluctuations within SC-LRPA are reliable.

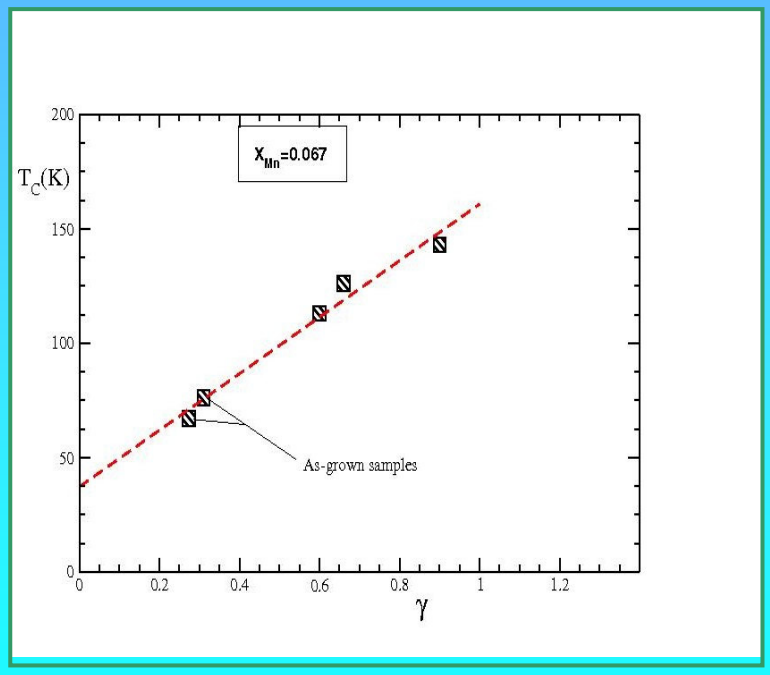
3-Effects of compensating defects.

a- Experimental results. (*Data from Edmonds et al. Nottingham*).

Variation of T_C for a fixed total density of Mn^{2+} after different annealing treatment for $Ga_{1-x}Mn_xAs$. The <u>total</u> Mn concentration is:

$$x_{Mn} = 0.067 \pm 0.003 = (15 \pm 1)10^{20}\ cm^{-3}$$

n_h (10^{20} cm $^{-3}$)	T_C (K)	détails
4.1 +/- 0.50	67	As grown
9.0 +/- 0.90	113	6hrs@180 °C
10.0 +/- 1.0	126	15hrs@180 °C
13.5 +/- 2.0	143	140hrs@180 °C
4.6 +/- 0.50	76	As grown



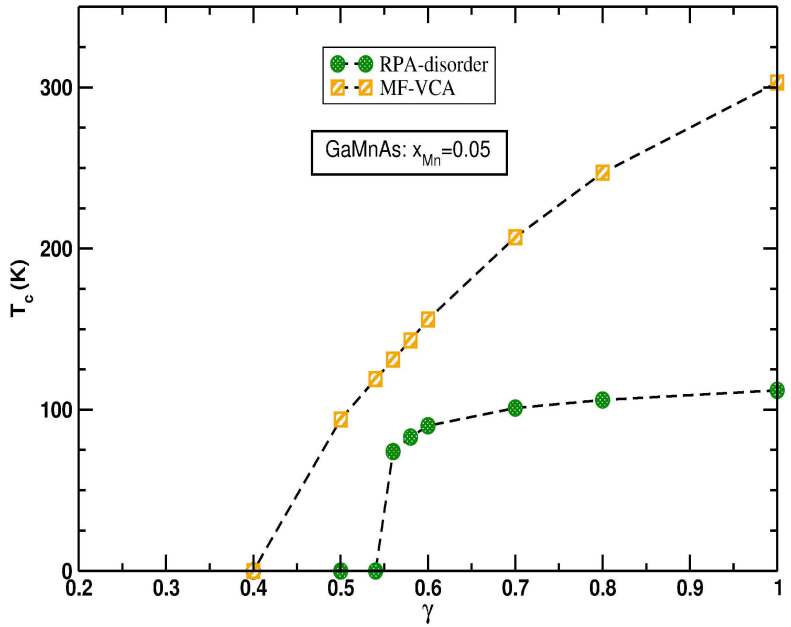
<u>Conclusion</u> :

*T_C varies in a significant manner from **67 K** to **143 K** depending on the history sample (annealing conditions).*

b- Effects of As anti-sites.

We assume that Mn(Ga) density is fixed x_{Mn} *and we vary the density* y_{As} *of As anti-sites :* $(Ga_{1-x_{Mn}-y_{As}}\ Mn_{x_{Mn}}\ As_{y_{As}})As$. *As on Ga sublattice is double donor, the density of holes is,*

$n_h = x_{Mn} - 2y_{As}$ *We introduce the reduced variable* $\gamma = \dfrac{n_h}{x_{Mn}}$



✓ *Weak variation of* T_C *with* γ *for* $\gamma >$ **0.60**

✓ *For* $\gamma <$ **0.55** *the ferromagnetism becomes unstable, the super-exchange dominate in the nearest neighbour exchange (frustration).*

✓ *Simple theory RKKY MF-VCA predicts that* $T_C = x^{4/3}\ \gamma^{1/3}$ *inconsistent with our results and experiments.*

We can not explain the experimental results by assuming that As anti-sites is the dominating mechanism of compensation.

c- Effects of Mn interstitials (Mn(I)).

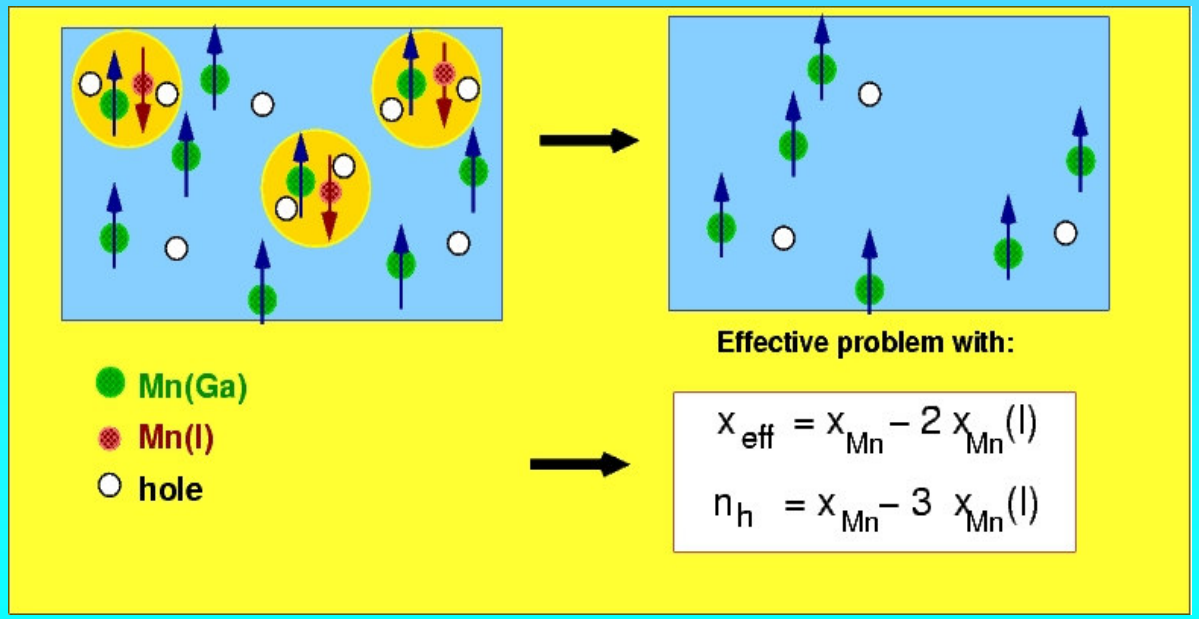
✓ *It is energetically more favourable for Mn(I) to be located near Mn(Ga). The coupling is **strongly** antiferromagnetic: reduction of Mn(Ga) magnetically active (J Masek and F. Maca PBR 2004).*

✓ *Mn(I) is a double donor: reduction of the carrier density.*

✓ *After annealing Mn(Ga)-Mn(I) pairs break and release carriers and increase active Mn(Ga).*

✓ *The problem reduces to an effective model of* $x_{eff} = x_{Mn} - 2x_{Mn}(I)$ *interacting active Mn with a hole density*

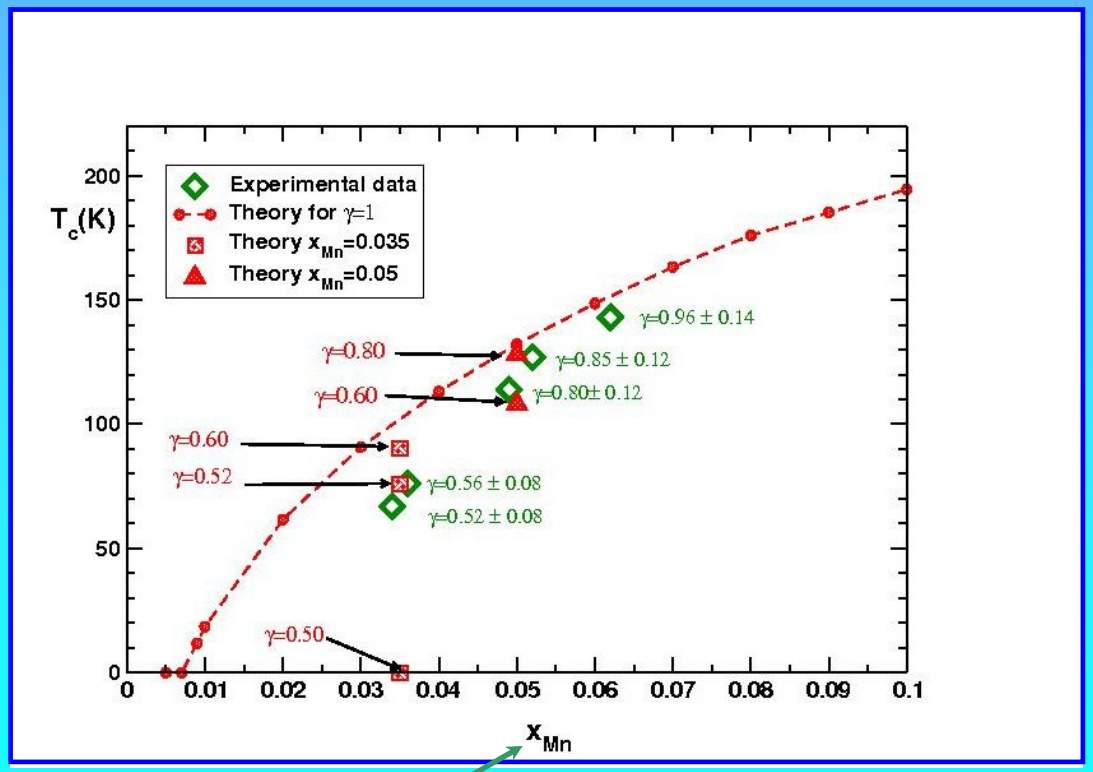
$$n_h = x_{Mn} - 3x_{Mn}(I)$$



d- Comparison between experiment and theory.

For each sample to calculate T_c we use the following expressions:

$$x_{eff} = \frac{x_{Mn} + 2n_h}{3} \quad et \quad \gamma_{eff} = \frac{3n_h}{x_{Mn} + 2n_h}$$

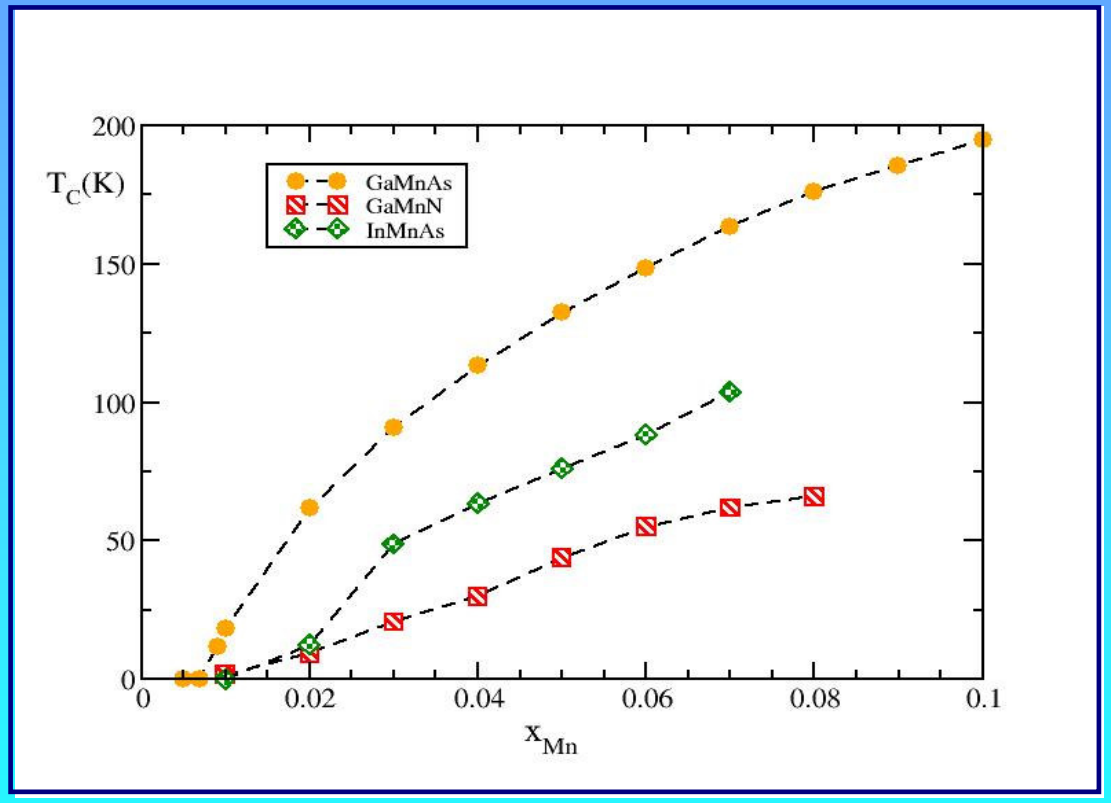


x_{eff}

- ✓ *Samples with highest T_C are in very good agreement with the calculations done for $\gamma = 1$.*
- ✓ *For « as-grown » samples we also reproduce Tc by taking into account that $\gamma < 1$.*
- ✓ *This study confirms that the dominating mechanism of compensation is due to Mn interstitials.*
- ✓ *The theoretical curve ($\gamma = 1$) allows to provide a good estimate of the value of TC for each sample :*

$$T_C = 649\,(x_{eff} - 0.0088)^{1/2}$$

4- Comparison between different DMS.



✓***GaMnAs*** *is the III-V material with the highest Curie temperature.*

✓ *Instead of the theoretical predictions based on MF-VCA calculations (Dietl et al.) that* $T_C = 600\ K$ *for* $x_{Mn} = 6\%$ ***GaMnN*** *has a very small* T_C*. In spite of a very strong nearest neighbour coupling (10 times that of* ***GaMnAs****)*

✓***InMnAs*** *exhibit intermediate Curie temperatures*

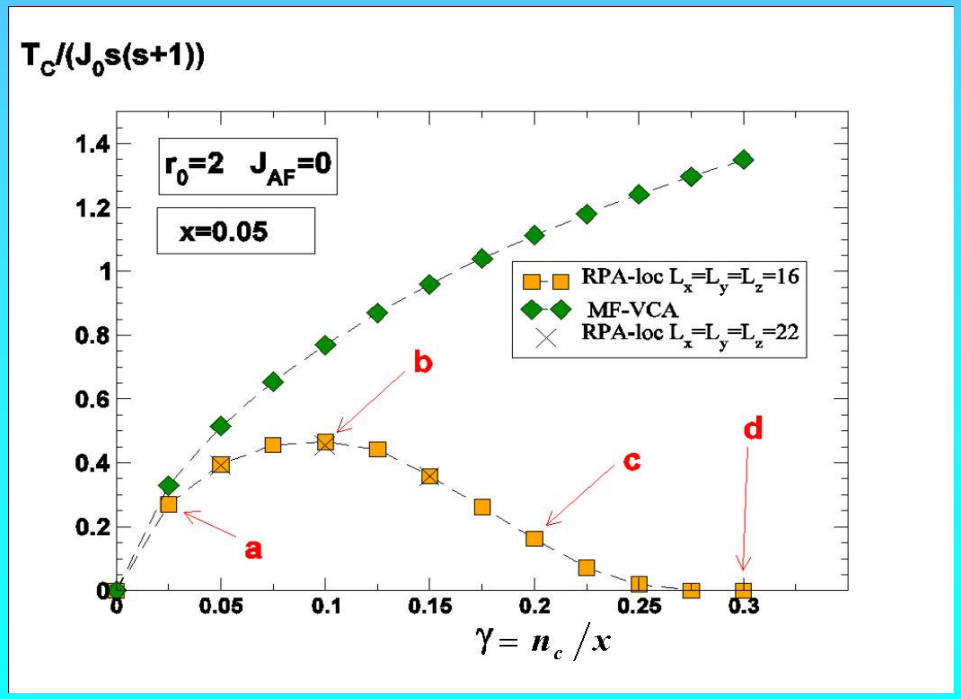
5- Are RKKY couplings appropriate in DMS?

In many model based studies the couplings are considered to be of RKKY type (**perturbative** treatment of the coupling between impurity and valence band). Additionally the Heisenberg Hamiltonian is usually treated within MF-VCA

We consider the following case:

$$J_{ij} = J_0 \exp(-\frac{r}{r_0})\left(\frac{\sin(2k_F r) - 2k_F r\cos(2k_F r)}{r^4}\right) + J_{ij}^{AF}$$

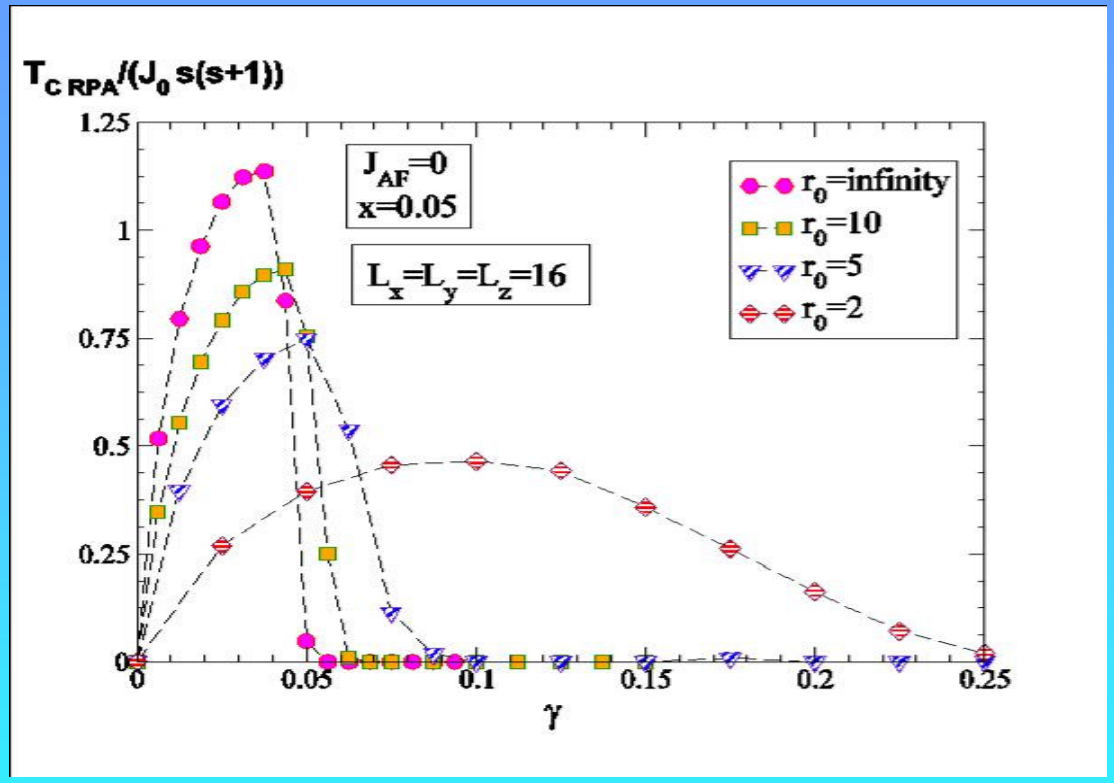
a- Effect of carrier density



R. Bouzerar, GB, and . Ziman PRB (2006)

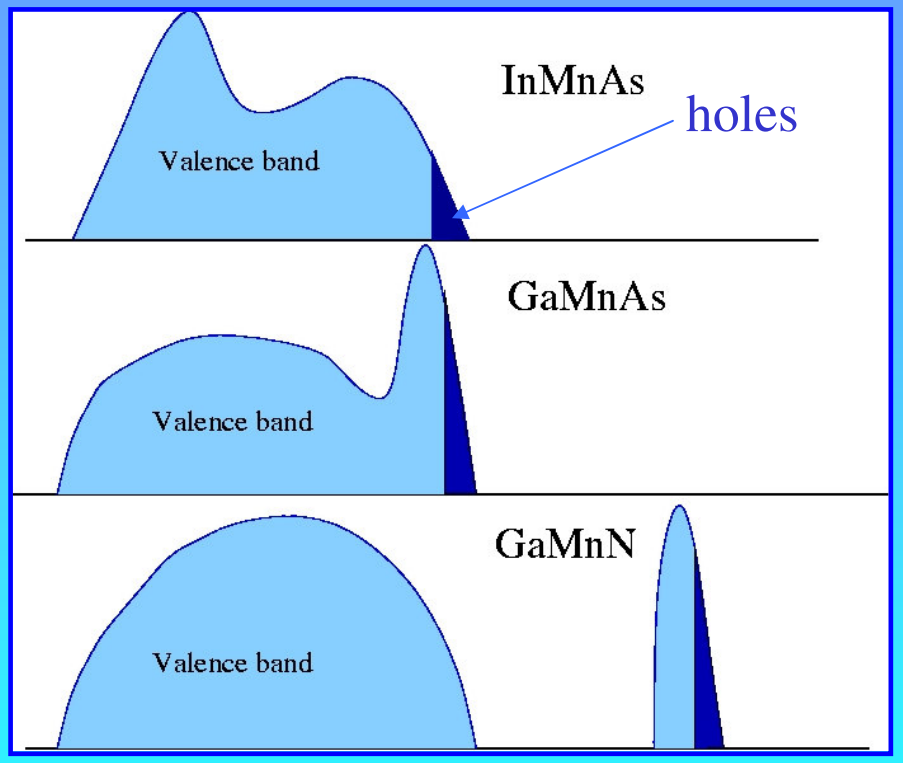
- *In contrast to MF-VCA (Priour-Das Sarma) T_C within SC-LRPA is much smaller: disorder and thermal fluctuations should be treated properly.*
- *The stability region of ferromagnetism is very narrow. In spite of the presence of the cut-off,frustration effects are still very efficient to suppress ferromagnetism and probably lead to a SG phase*
- *T_C exhibit a maximum at very low carrier density. It is qualitatively different from MF-VCA.*
- *The results are inconsistent with the experimental observation of ferromagnetism for γ close to 1.*

b- Influence of the cut-off



- *For the pure undamped RKKY case the region of stability of ferromagnetism is **extremely narrow** (combined effects of frustration, disorder and thermal fluctuations)*
- *With increasing the cut-off the region of stability increases (suppression of the oscillating tail) but the maximum value of TC is reduced.*
- *Even for relatively strong value of the cut-off parameter the stability region remains relatively narrow.*

6- Which relevant parameters control T_C ?



✓ *InMnAs*:

- *The exchange couplings are closer to a standard RKKY standard (oscillations).*
- *Because of the oscillations of the couplings T_C will not be so large.*

✓ *GaMnAs :*

- *The impurity band is well defined.*
- *Effects of resonances on the exchange integrals (suppress the RKKY oscillation)*

✓ *GaMnN :*

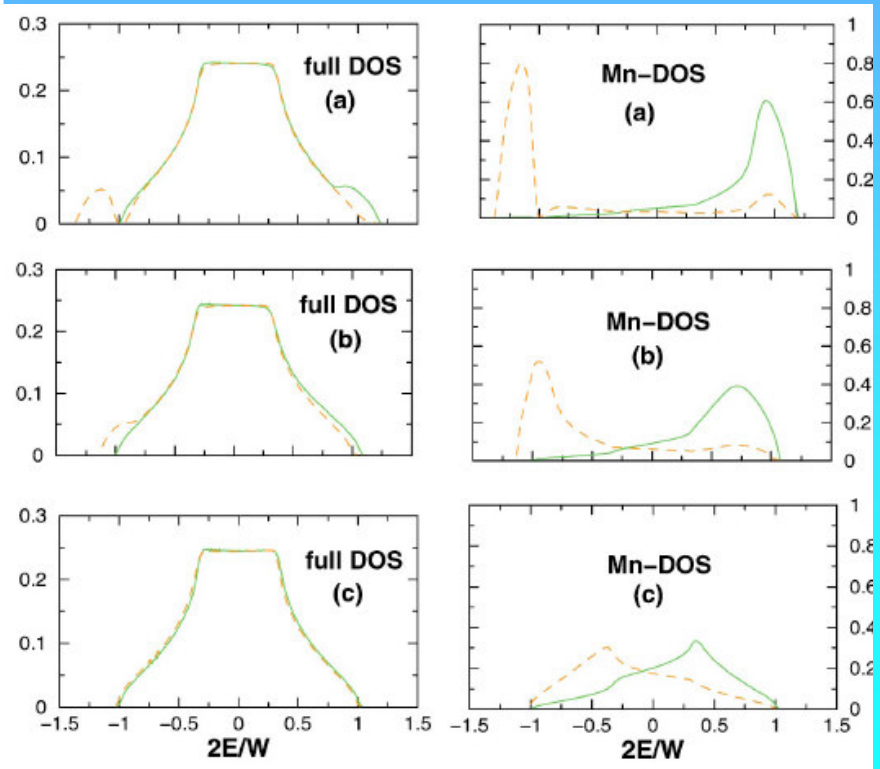
- *The impurity band is located in the middle of the gap between VB-CB.*
- *The couplings are strongly damped* ***(very short range)***

Both (i) the position of the impurity band with respect to the top of the VB and (ii) the density of carriers play a crucial role.

7- V-J_{pd} model: a good candidate for model studies

$$H = \sum_k t_{ij}\ c_{i\sigma}^{+} c_{j\sigma} + \text{hc} + \sum_{i \in I} J_{pd}\ S_i \cdot s_i + \sum_{i \in I} V\ n_i$$

a- DOS



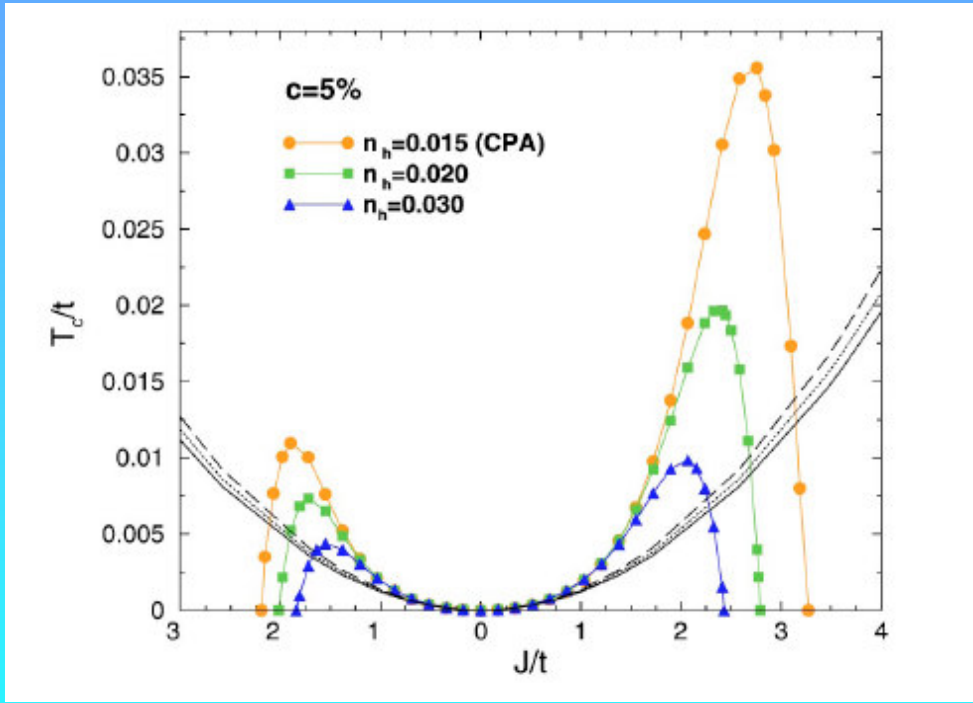
In this approach the disorder and the multiple scatterings on the magnetic impurities are treated within CPA treatment. The calculation were performed for W=0 .

(a) Jpd=3.45 t; (b) Jpd= 2.33 t and (c) Jpd=0.86t. ;

x=5% of impurities and the impurity spin S=5/2

GB, J. Kudrnovsky and P. Bruno PRB (2003)

b- Mean Field Curie temperature



✓ *The exchange couplings were calculated within CPA (disorder is partly included)*

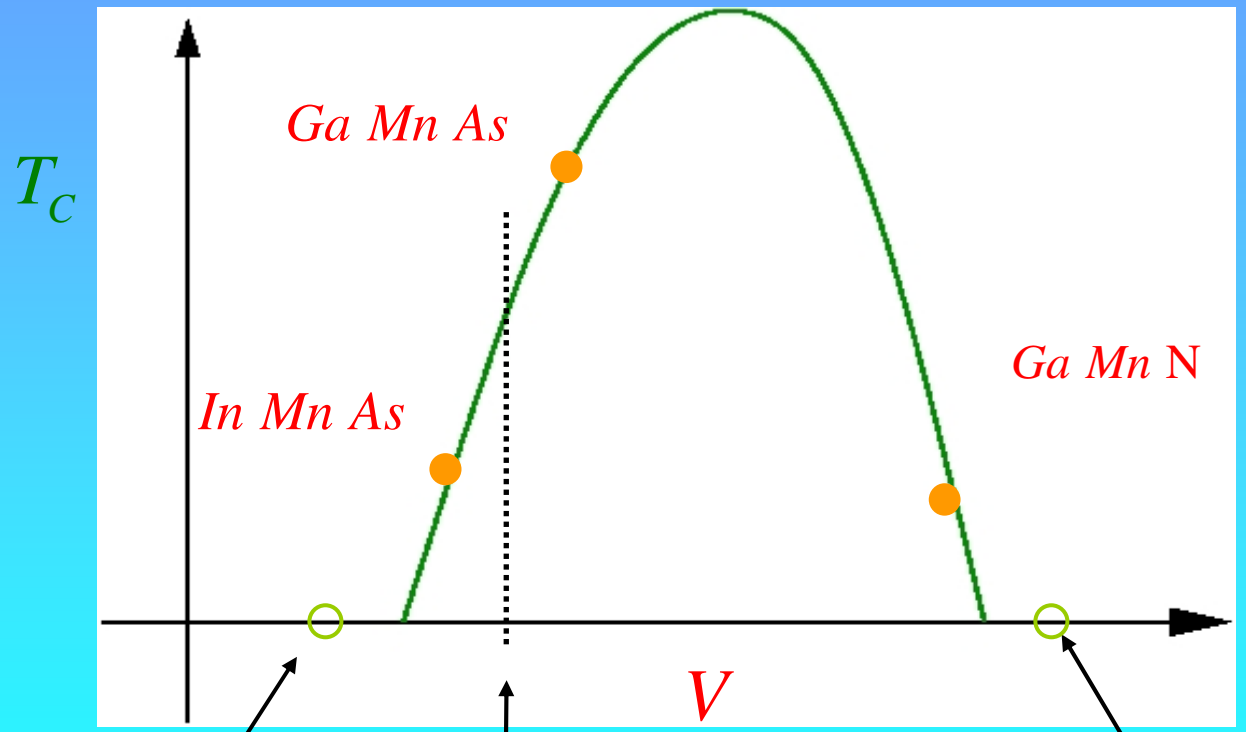
✓ *We recover the RKKY limit for very weak coupling Tc scales with* $J_{pd}^{\ 2}$

✓ *TC exhibit a well defined peak corresponding to the pre-formation of the impurity band. Disorder enhances the the MF Curie temperature.*

✓ *For strong coupling limit the Curie temperature vanishes.*

Remark: (i) The couplings should be now calculated with an exact treatment of disorder and (ii) The Heisenberg model diagonalized within SC-LRPA to show the effects of both thermal fluctuations and disorder (R. Bouzerar et al. work in progress)

We maintain Jpd, t constant and vary V to tune the position of the impurity band with respect to the top of the valence band.



RKKY oscillation

Impurity band is formed

Superexchange dominate

IV- Conclusions.

- The SC-LRPA is reliable to study ferromagnetism in disordered systems.
- The detailed study of GaMnAs has provided a very good agreement with the experimental results (*before and after annealing*) and shows that ab-initio TB-LMTO are reliable.
- The theory is *general* and can be applied to various systems (d^0 ferromagnetism, *manganites, double perovskites,....)*
- Without any change one can include the effects of *correlations* and *inhomogeneities* in the disorder.
- From CPU point of view the SC-LRPA calculations which agree with Monte-Carlo are at least *3 orders of magnitude* faster.
- Under study: *magnetic excitations, magnetizations as a function of temperature,...*
- *The study of the V-Jpd model is in progress, it should allow to provide a coherent picture of ferromagnetism in DMS.*