EXCHANGE INTERACTIONS IN DILUTED MAGNETIC SEMICONDUCTORS: effect of disorder on Curie T_c

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OUTLINE

- **Introduction**
- **Electronic structure**
- **Exchange interactions and their properties**
- **The alloy Curie temperature**
- **Conclusions**

INTRODUCTION

Aim: determination of **exchange interactions** and critical temperatures of **diluted magnetic semiconductors** from first principles which takes into account the **disorder** exactly

- **Empirical models**: kinetic exchange model with empirically fitted relevant parameters (J_{pd}, carrier density) in the MFA $\Rightarrow$ **full** neglect of disorder (electronic structure and Curie temperature)

- **Realistic models**: Heisenberg models with parameters derived from realistic calculations (LSDA) which include the effect of **alloying** $\Rightarrow$ the resulting Heisenberg model is studied in approximations **neglecting** disorder (VCA/ ordered supercells)

- Effect of **disorder**: low impurity concentration, localized magnetic interactions and their strong directional character combined with randomess $\Rightarrow$ (magnetic) **percolation** is possible

- **Present approach**: two-step approach suggested by Liechtenstein (1987) and generalized to **alloys** $\Rightarrow$ **alloy** total energy is mapped onto the classical **random Heisenberg model** studied by methods of statistical mechanics (**Monte Carlo** simulations)

1st step: ELECTRONIC STRUCTURE

$(Ga_{1-x-y}Mn_xAs_y)As$, $(Ga_{1-x}Mn_x)N$, $(Zn_{1-x}Cr_x)Te$)

- **TB-LMTO**: scalar-relativistic, ES-interstitials for a good space-filling (A^{III}-B^{V}-E_1-E_2, A^{II}-B^{VI}-E_1-E_2)

- **Green function** method and the **CPA** are used include the **disorder** (arbitrary concentration)
  - magnetic **atoms** (subst/interst)
  - native As-**antisites**
  - **co-doping** by various (nonmag) defects

- **Densities of states**: total and atom-resolved

$$\bar{g}(E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\,\bar{G}(E^+), \quad \bar{g}^Q(E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\;\bar{G}^Q(E^+)$$

$\bar{G}(z)$ – **configurationally** averaged GF

$\bar{G}^Q(z)$ – **conditionally** averaged GF $\Rightarrow$ average over all configs with atom Q fixed at a given site

- **Bloch spectral functions** $\Rightarrow$ 'bands' in alloys

$$A(\mathbf{k}, E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\,\langle G(\mathbf{k}, E + i\delta)\rangle$$

crystals: $A(\mathbf{k}, E) = \sum_i \delta(E - E_i(\mathbf{k}))$

random alloys:
- **weak** disorder $\Rightarrow$ broadened and shifted δ-peaks
- **strong** disorder $\Rightarrow$ non-quasiparticle behaviour

2nd step: MAPPING TO HEISENBERG MODEL

- The **change** of total energy connected with rigid **rotations** of the spin-directions at sites i, j is calculated in the LSDA and **mapped** onto effective **Heisenberg model** (with classical spins)

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

$\mathbf{e}_i$, $\mathbf{e}_j$ – unit vectors of the **local** magnetic moments
J_{ij} – **random** effective exchange interactions between magnetic atoms at sites i, j

- Effective **exchange parameter**: sum of exchange interactions acting on a given magnetic atom

$$J_i = \sum_{j \neq i} J_{ij} \quad \Rightarrow \quad \text{estimate of } \mathbf{T_c^{MFA}}$$

- **Adiabatic approximation**: $E(\mathbf{q}) \ll \Delta_{\mathrm{exc}}, W$

- **Magnetic-force theorem** and the **Lloyd formula** are used to obtain explicit expression for J_{ij}

- Generalization to **random alloys** $\Rightarrow$
the **change** of total energy connected with rigid **rotations** of two spins at sites i, j **embedded** in the effective medium is determined using the **CPA** and the **vertex-cancellation theorem** (P. Bruno)

EXCHANGE INTERACTIONS IN ALLOYS

Averaged pair interactions in **random** alloys are:

$$\bar{J}_{i,j}^{QQ'} = \frac{\mathrm{Im}}{4\pi} \int^{E_F} \mathrm{tr}_L \left[\Delta_i^Q \, \bar{\mathbf{g}}_{i,j}^{QQ',\uparrow}(z) \, \Delta_j^{Q'} \, \bar{\mathbf{g}}_{j,i}^{Q'Q,\downarrow}(z) \right] \mathrm{d}z$$

tr_L - trace over orbital index, $\quad z = E + i\delta$

Δ_i^Q - exchange **splitting** on magnetic atom Q

$\bar{\mathbf{g}}_{i,j}^{QQ',\sigma}(z)$ - **conditionally-averaged** Green function matrices: atoms Q, Q' are **fixed** at i, j

$\bar{\mathbf{g}}_{i,j}^{QQ',\sigma}(z) = f_i^{Q,\sigma}(z) \, \bar{\mathbf{g}}_{i,j}^{\sigma}(z) \, f_j^{Q',\sigma}(z)$

$f_i^{Q,\sigma}$ - **enhancement**: $f_i^{Q,\sigma} = \bar{\mathbf{g}}_{ii}^{Q,\sigma} / \bar{\mathbf{g}}_{ii}^{\sigma}$ (spin/$\mathrm{E_F}$)

$\bar{J}_{i,j}^{QQ'}$ are **robust** with respect to system randomness:

– carrier density & concentration trends are **reliably** described by the **CPA** $\Rightarrow$ medium which **mediates** interactions (Fermi surface topology)

– the **effect** of fluctuations in Green functions due to the **local** environment is small for **averaged** $\bar{J}_{i,j}^{QQ'}$ in **metallic** sample ($\mathrm{E_F}$ lies inside VB)

– **low-concentrations** $\Rightarrow$ random alloys (CPA)

– **correlated** impurities $\Rightarrow$ embedded cluster???

Properties of exchange interactions $\bar{J}_{i,j}^{QQ}$:
$\Rightarrow$ differ from the conventional RKKY interactions:

- **Discrete** character due to real lattice
- modification of **amplitudes/phases** (factor $f_i^{Q,\sigma}$)
- **Asymptotic behavior** for $\mathbf{d} = \mathbf{R}_i - \mathbf{R}_j \to \infty$

$$\bar{J}_{\mathbf{d}}^{Q,Q} \propto \; \mathrm{e}^{-\,\boldsymbol{\lambda}^{\uparrow}\cdot\mathbf{d}} \cdot \mathrm{e}^{-\,\boldsymbol{\kappa}_{\mathrm{F}}^{\downarrow}\cdot\mathbf{d}} \; \frac{\sin(\mathbf{k}_{\mathrm{F}}^{\uparrow}\cdot\mathbf{d} + \Phi^{\uparrow} + \Phi^{\downarrow})}{|\mathbf{d}|^3}$$

$\boldsymbol{\lambda}^{\uparrow}$ - damping due to **alloy disorder** (de Gennes)
$\boldsymbol{\kappa}_{\mathrm{F}}^{\downarrow}$ - damping due to **halfmetallic** behavior
(Fermi energy in the gap of minority states)

- both dampings are **missing** in the model with ideal semiconductor host

- strong directional dependence of $\bar{J}_{\mathbf{d}}^{Q,Q}$ due to the topology of the host semiconductor alloy Fermi surface

- alloy disorder is very anisotropic inside Brillouin zone (anisotropic dampings $\boldsymbol{\lambda}^{\uparrow}$ and $\boldsymbol{\kappa}_{\mathrm{F}}^{\downarrow}$)

- Thermodynamic **properties** of TM-ferromagnets (**Fe,Co**), f-metal ferromagnets (**Gd,Eu**), magnetic **overlayers** on non-magnetic substrates, **alloys** of TM-ferromagnets and noble metals were **all** successfully studied using the **two-step** approach

THE ALLOY CURIE TEMPERATURE

- **Problems: randomness** in exchange interactions (J or 0) and **fulfilment** of the **Goldstone** theorem:

$$\bar{J}_i = \sum_{i \neq j} \bar{J}_{i,j}$$

$\Rightarrow$ The **simplest** way how to get around the above **problems** is to use the **VCA** (virtual crystal approximation, averaged lattice) while **statistical treatments** are performed on different **levels** of sophistication (MFA, RPA, MC)

A. **Nonrandom lattice**

- **MFA-VCA**: Dietl, MacDonald and many others

$$k_{\mathrm{B}} T_{\mathrm{C}}^{\mathrm{MFA}} = \frac{2\mathbf{x}}{3} \sum_{i \neq 0} \bar{J}_{0i}^{QQ}$$

- **RPA-VCA**: Bouzerar *et al.*, 2003

$$\left(k_{\mathrm{B}} T_{\mathrm{C}}^{\mathrm{RPA}}\right)^{-1} = \frac{3}{2\mathbf{x}} \frac{1}{N} \sum_{\mathbf{q}} \left[\bar{J}(\mathbf{0}) - \bar{J}(\mathbf{q})\right]^{-1} ,$$

$\bar{J}(\mathbf{q})$ denotes the lattice **fourier transform** of $\bar{J}_{ij}^{Q,Q}$:

$$\bar{J}(\mathbf{q}) = \sum_{i(i \neq 0)} \bar{J}_{0i}^{Q,Q} \cdot \mathrm{e}^{i\mathbf{q} \cdot \mathbf{R}_{0i}}$$

- **Monte Carlo (MC-VCA)**: ordered network of magnetic atoms $\Rightarrow$ randomness is **neglected**

B. **Random lattice**

- **Analytical** theories ⇒ local environment effects has to be **included** to fulfil Golstone theorem: **RPA-CPA** (Bouzerar & Bruno, 2002) with the randomess **included** in the CPA ⇒ clustering/SRO effects are **neglected**

- **Semianalytical** theory ⇒ disorder treated exactly in the real-space (MC) while **spin-fluctuations** are included in the **RPA** (Bouzerar *et al.*, 2004) ⇒ cond-mat/0405322

- **Monte Carlo simulations** (random network): magnetic percolation, clustering and SRO effects can be **included**:

  A. *Empirical models*: Timm (2002), Zaránd (2004)
  B. *Ab initio models*: present & Sato *et al.*, (2004)

  - **Metropolis** algorithm employed
  - **randomly** distributed 8000-27000 magnetic atoms on fcc-lattice ⇒ finite size **scaling** approach used, **average** over 5 random configurations
  - up to **20 NN** exchange interactions included in the Heisenberg model (the shell convergence): **less** shells is needed for more localized exchange interactions (e.g. Mn-doped GaN)
  - the **cumulant crossing method** used to find T_c
  - extensive calculations ⇒ Bergqvist & Eriksson

CONCLUSIONS

- **two-step approach**: *ab initio* evaluation of the alloy **exchange interactions** combined with the Monte Carlo simulations on **random lattice** ⇒ a tool for **reliable** evaluation of **critical temperatures** of **random** alloys with **large local magnetic moments**

- values of exchange interactions are influenced by **number of carriers** and **strength of impurity scattering**:

A: **damping** of exchange interactions due to **alloy disorder** and **half-metallic** behavior
⇒ **short-range character** of interactions
B: **directional** character of exchange interactions

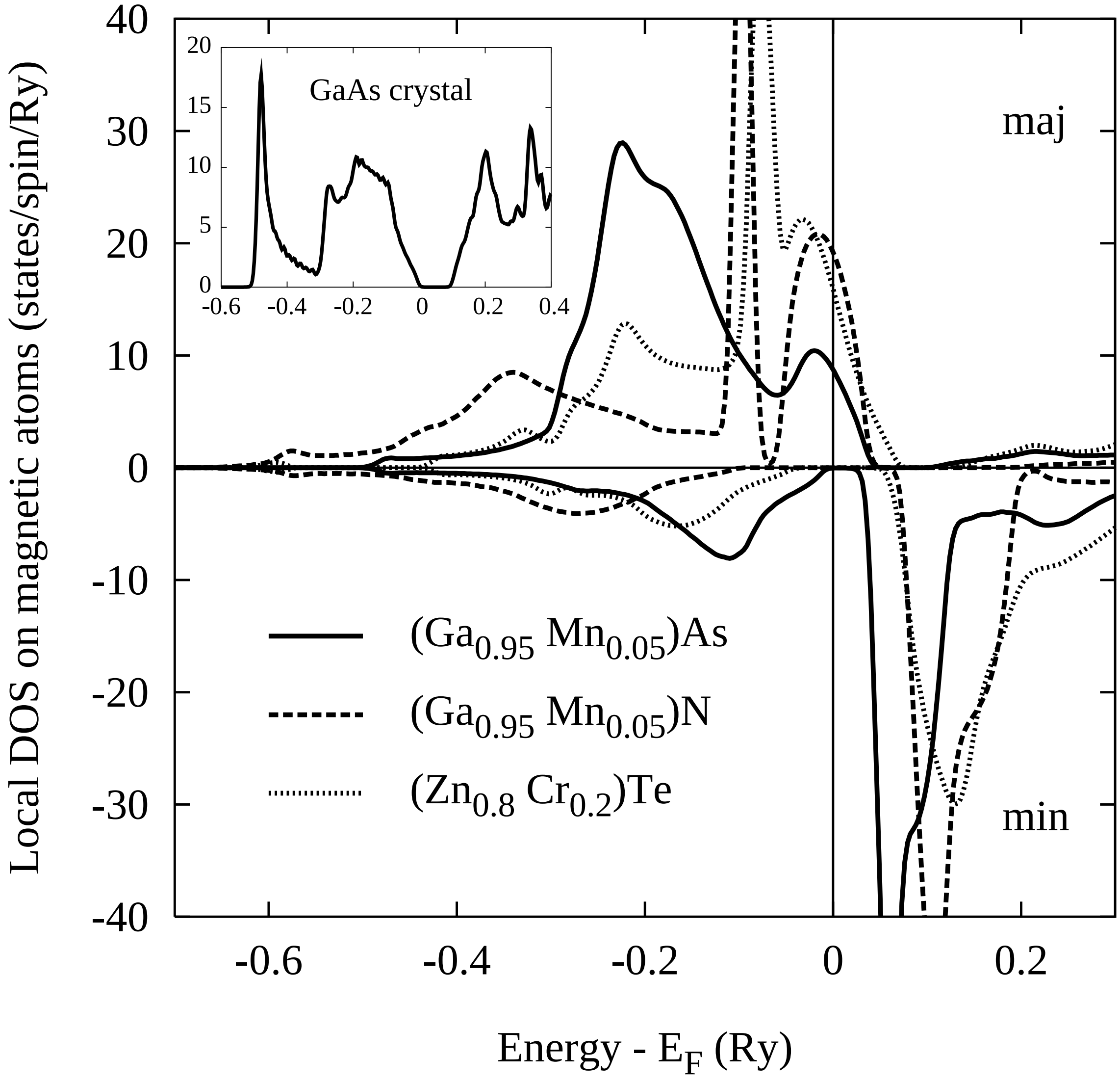
- randomness + A + B ⇒ **magnetic percolation** strongly reduces values of **critical temperatures** as compared to models neglecting **disorder**

- calculated Curie temperatures compare well with available **experimental** data and explain strong **dependence** of $\mathbf{T_c}$ on the sample preparation ⇒ **distribution** of magnetic atoms on lattice

- $\mathbf{T_c}$**/conductivity** relation found in **experiment** (GaMnAs) was reproduced by the **theory** ⇒ carrier-mediated **ferromagnetism**

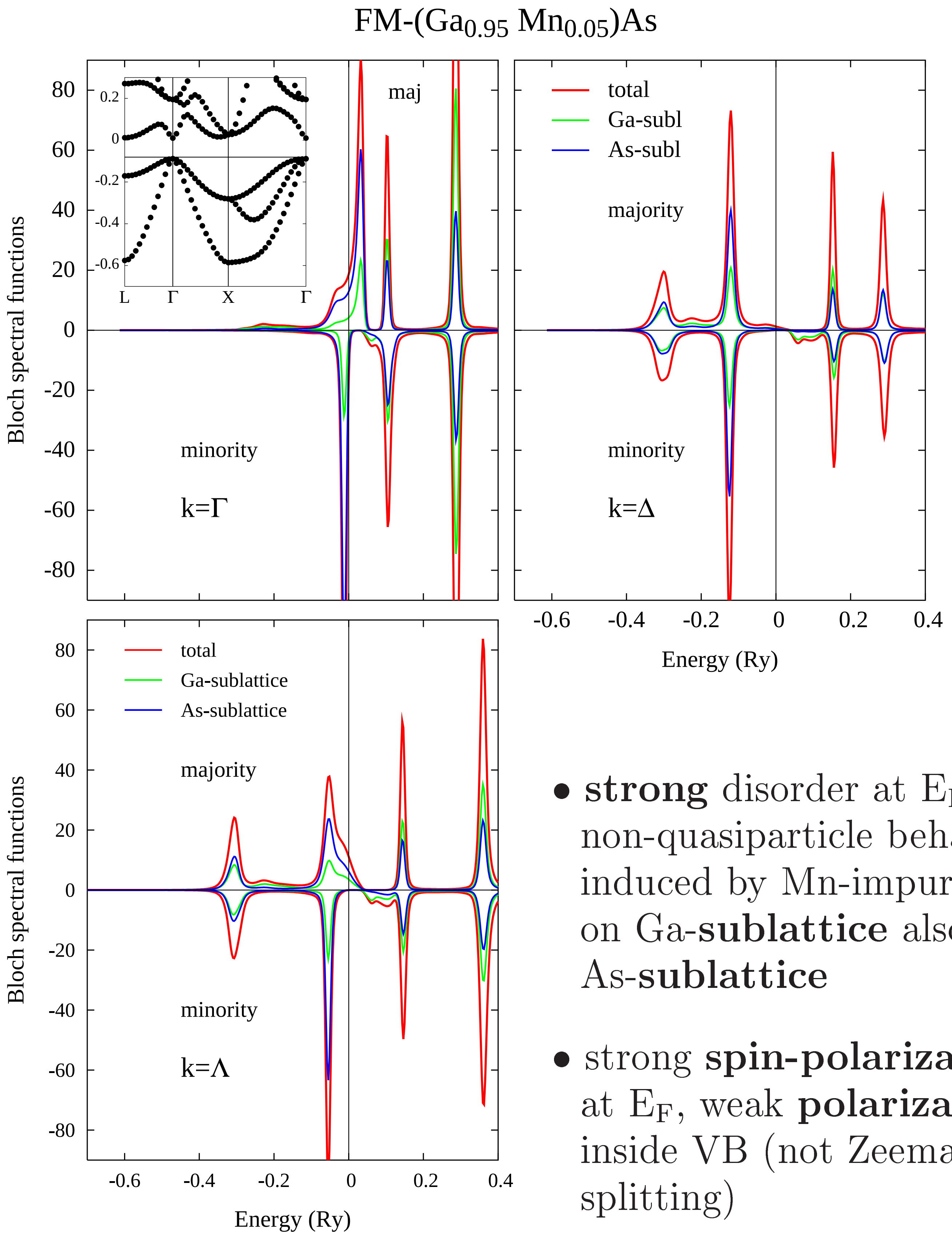
- approach allows for generalization to the case of **correlated ditributions** of magnetic atoms (determination of exchange interactions ???)

Spin-resolved local density of states on magnetic atoms in Mn-doped GaAs and GaN and Cr-doped CrTe



- **Local** density of states: $D^Q(E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{tr}\,\bar{G}^Q(E^+)$,
  $\bar{G}^Q(z)\rangle$ – **conditionally** averaged GF
  $\Rightarrow$ average over all configurations with magnetic atom Q fixed at a given site
- **halfmetallic** behavior of all alloys
- Fermi energy inside **majority** impurity bands but in the gap of **minority** bands

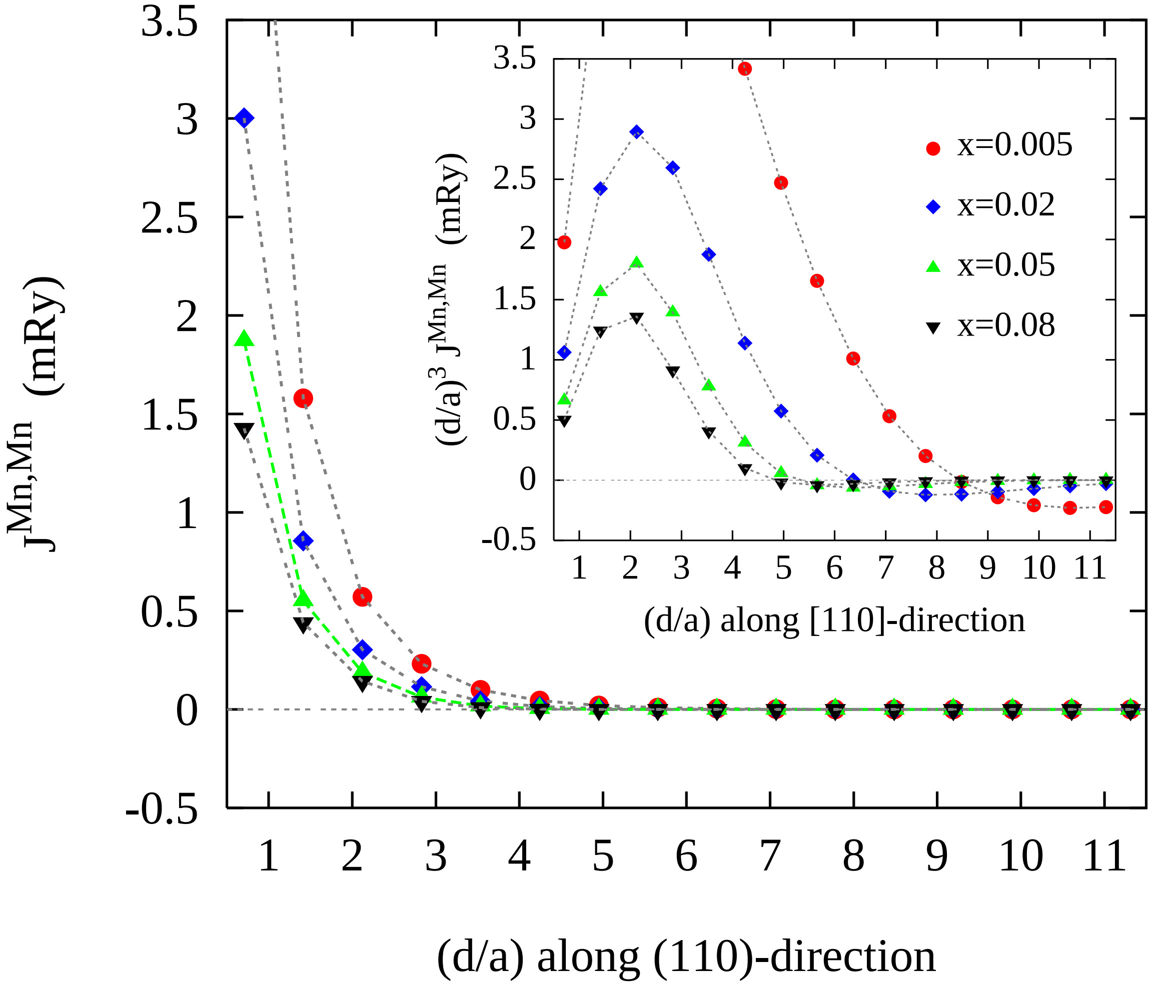
Spin-resolved Bloch spectral functions



- **strong** disorder at $E_F \Rightarrow$ non-quasiparticle behavior induced by Mn-impurities on Ga-**sublattice** also on As-**sublattice**
- strong **spin-polarization** at E_F, weak **polarization** inside VB (not Zeeman splitting)

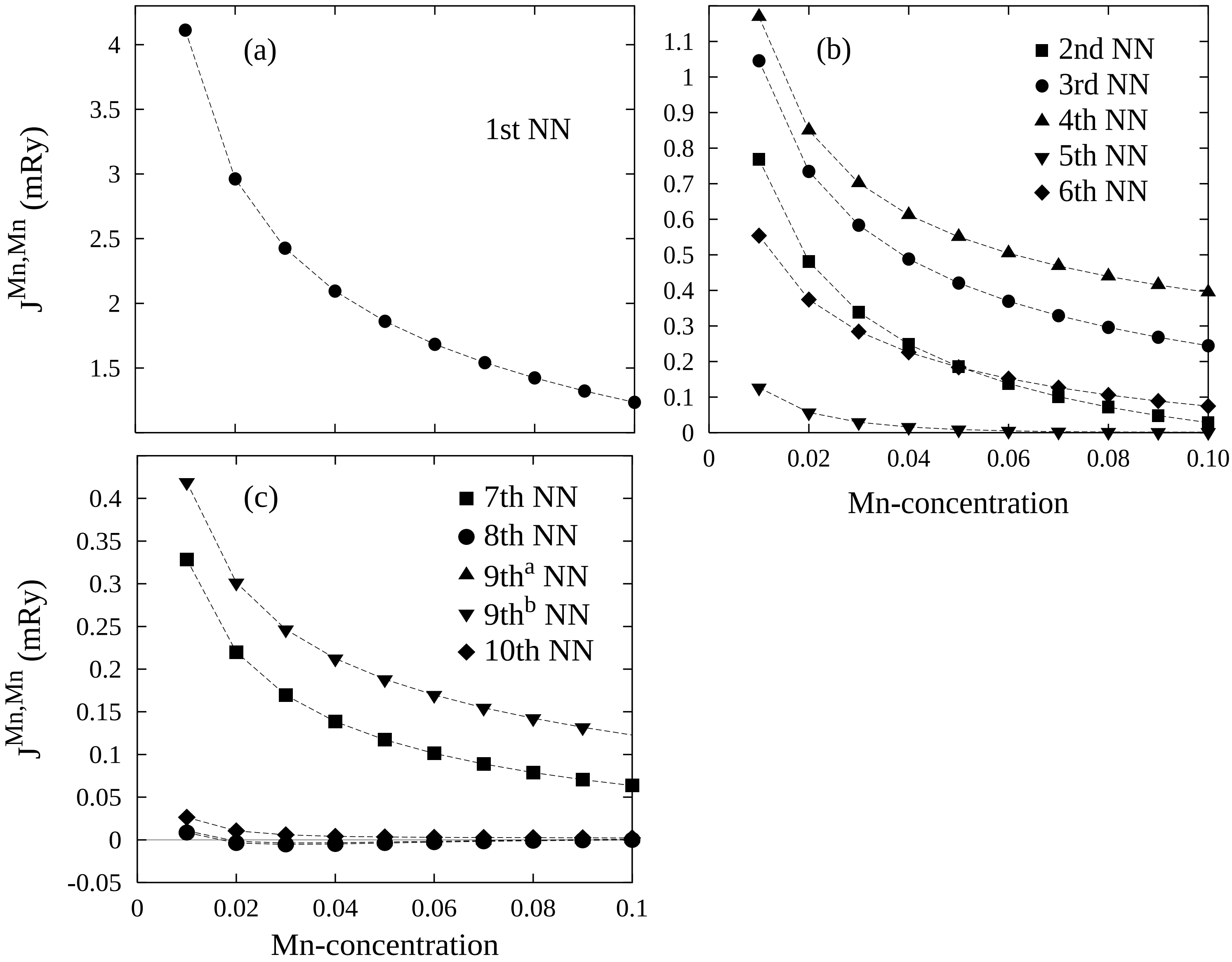
- **disorder** $\Rightarrow$ finite **carrier-lifetime** (Tc/ conductivity)

Dependence of exchange interactions on Mn-concentration in (Ga,Mn)As alloys



- exchange interactions are **reduced** with increasing Mn-concentration
- exchange interactions are (**exponentially**) damped with the distance
- period of oscillations **decrease** with concentration $\Rightarrow$ **size** of Fermi surface/ **carrier** concentration
- exchange interactions are **ferromagnetic** over distance **large** as compared to averaged distance between Mn-atoms $\Rightarrow$ ferromagnetism is **stabilized**

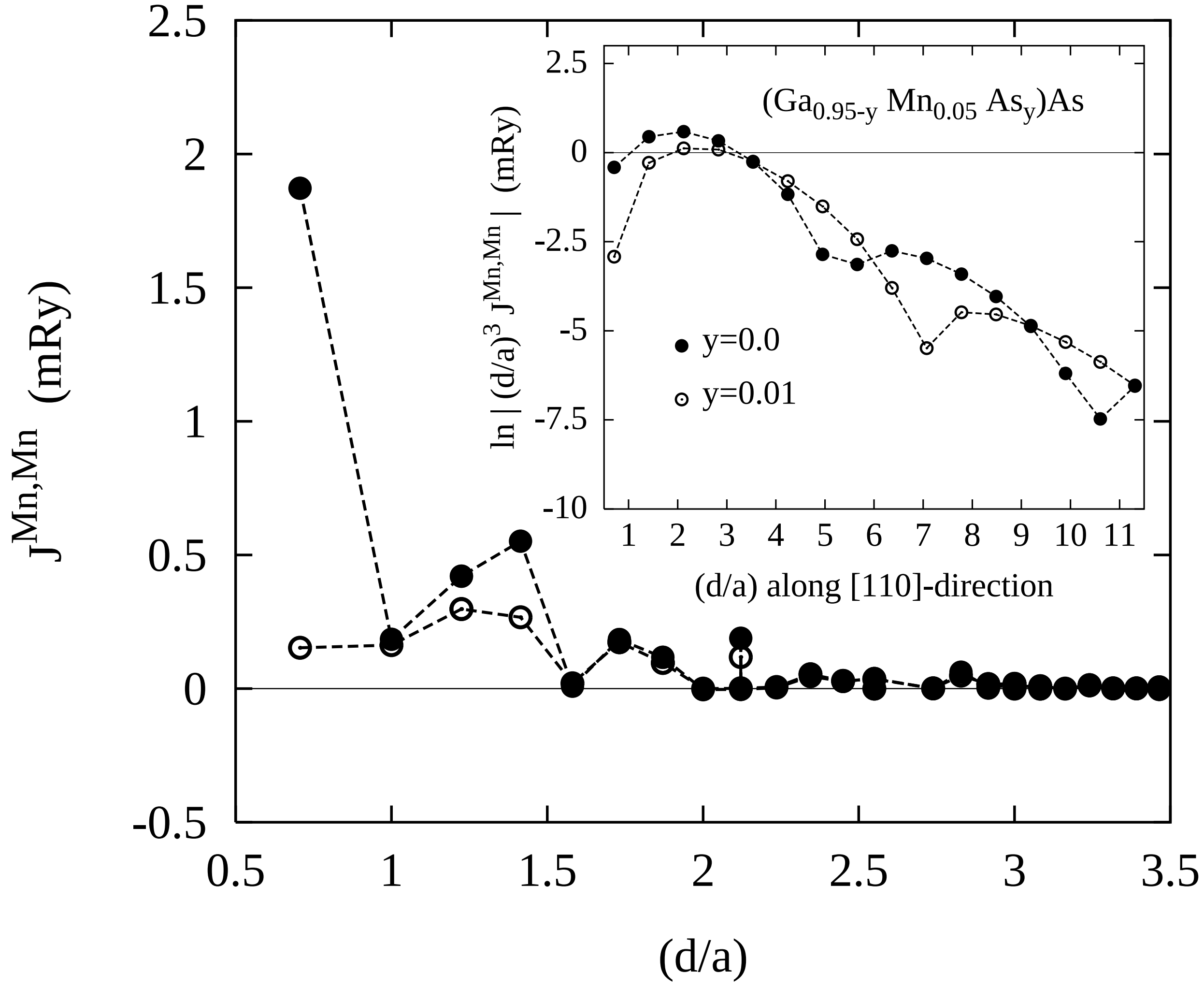
Dependence of exchange interactions on Mn-concentration in (Ga,Mn)As alloys: first 10-NN shells



- exchange interactions are **reduced** with increasing Mn-concentration

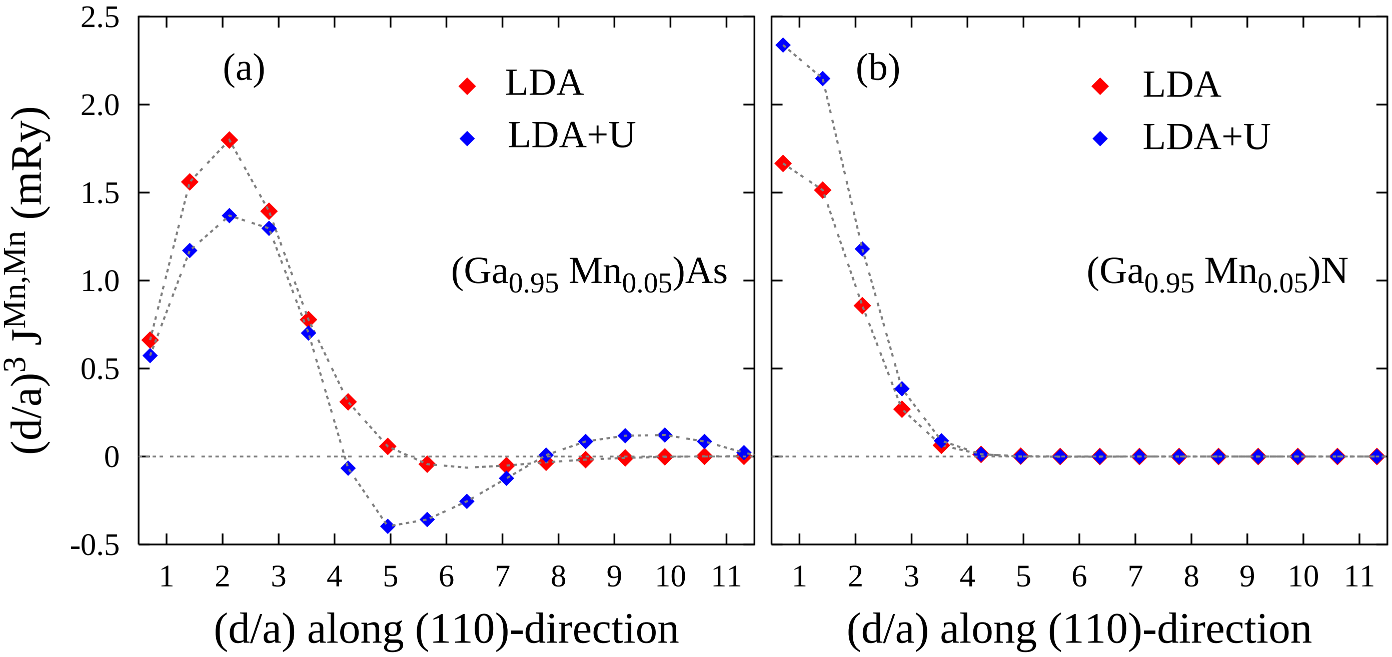
- exchange interactions are **ferromagnetic** over distance **larger** as compared to averaged distance between Mn-atoms $\Rightarrow$ ferromagnetism is **stabilized**

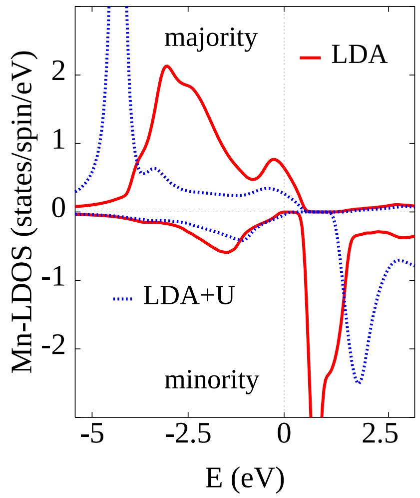
Dependence of exchange interactions on concentration of As-antisites in (Ga,Mn)As alloys



- exchange interactions are **reduced** with increasing concentration of As-antisites ⇒ ferromagnetism is **suppressed**
- exchange interactions are **exponentially** damped with the distance due to alloy **disorder** and **half-metallic** behavior
- periods of damped oscillations **increase** with reduced As-concentration ⇒ reduced **carrier** concentration

Effect of electron correlations on exchange interactions in (Ga,Mn)As alloys





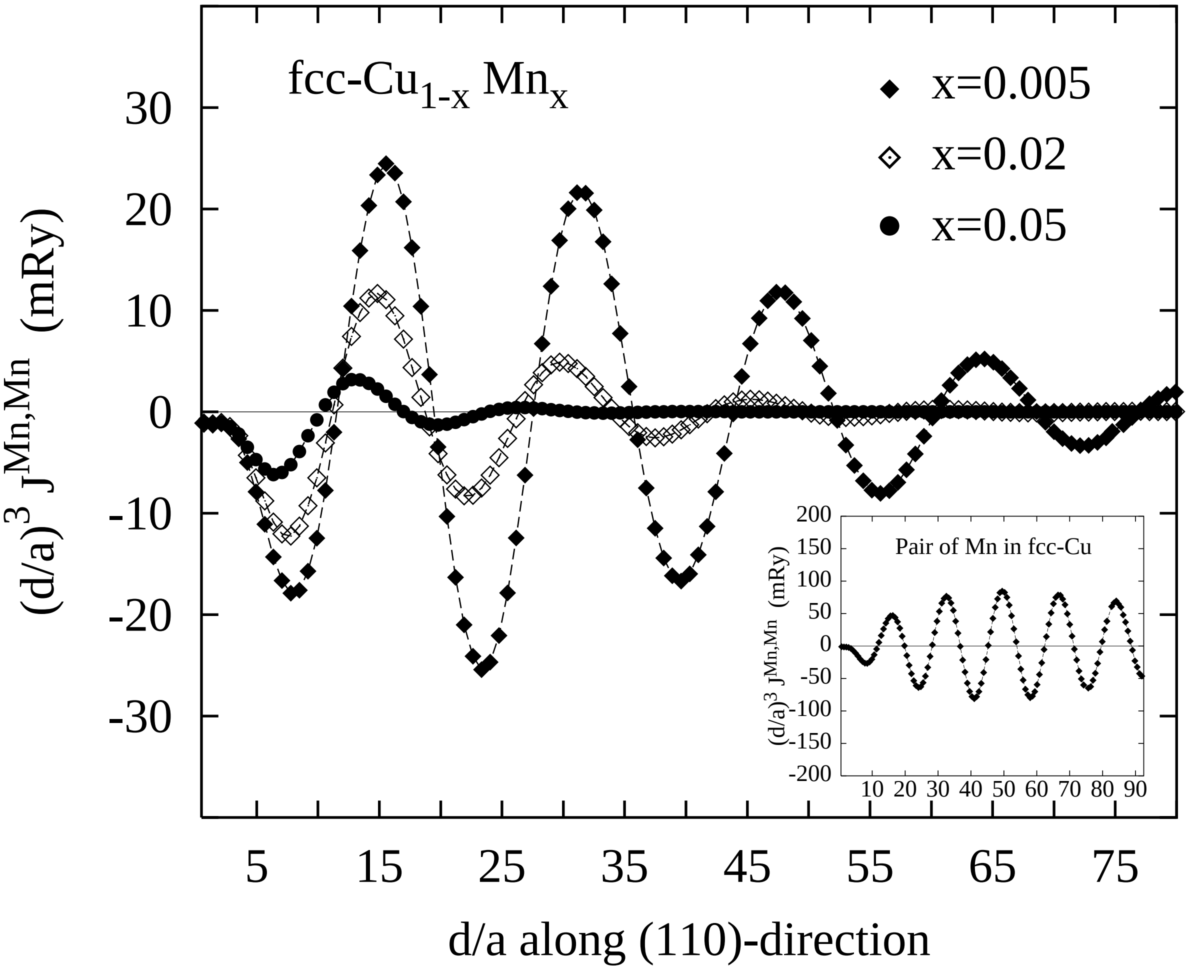
- electron correlations **suppress** Mn-*d* character at the Fermi energy ⇒ exchange interactions are **less damped**

- modified topology of the Fermi surface ⇒ period of damped oscillations are **changed**

- exchange interactions in Mn-doped GaN are damped **more strongly** than in Mn-doped GaAs

Concentration dependence of exchange interactions in fcc-$Cu_{1-x}Mn_x$ alloys

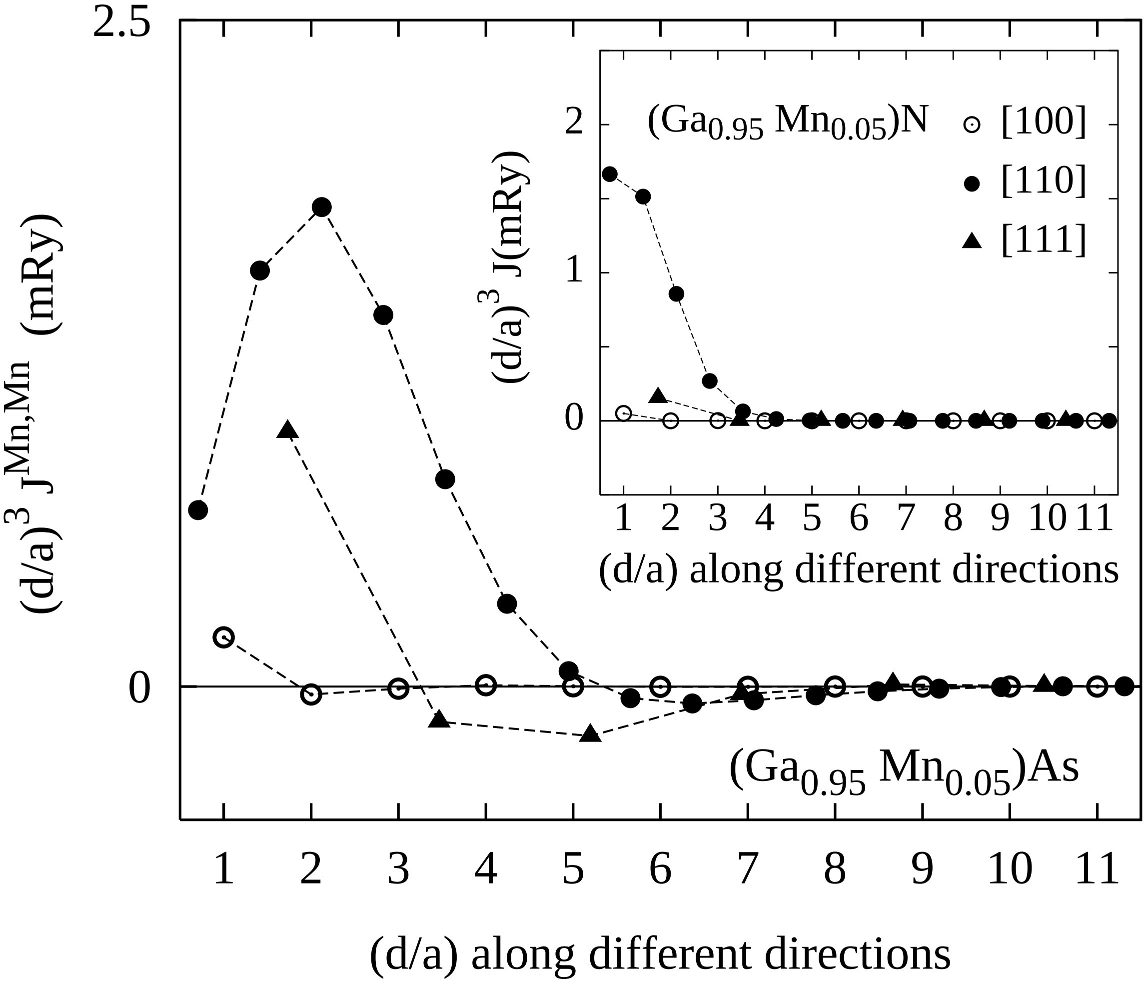
(multiplied by RKKY-factor $(d/a)^3$)



- **RKKY**-type behavior for very low concentrations
- exchange interactions are **exponentially** damped due to alloy **disorder**
- [110]-direction **dominates** for large distances

Directional dependence of exchange interactions in $(Ga_{0.95}Mn_{0.05})As$ and $(Ga_{0.95}Mn_{0.05})N$ alloys

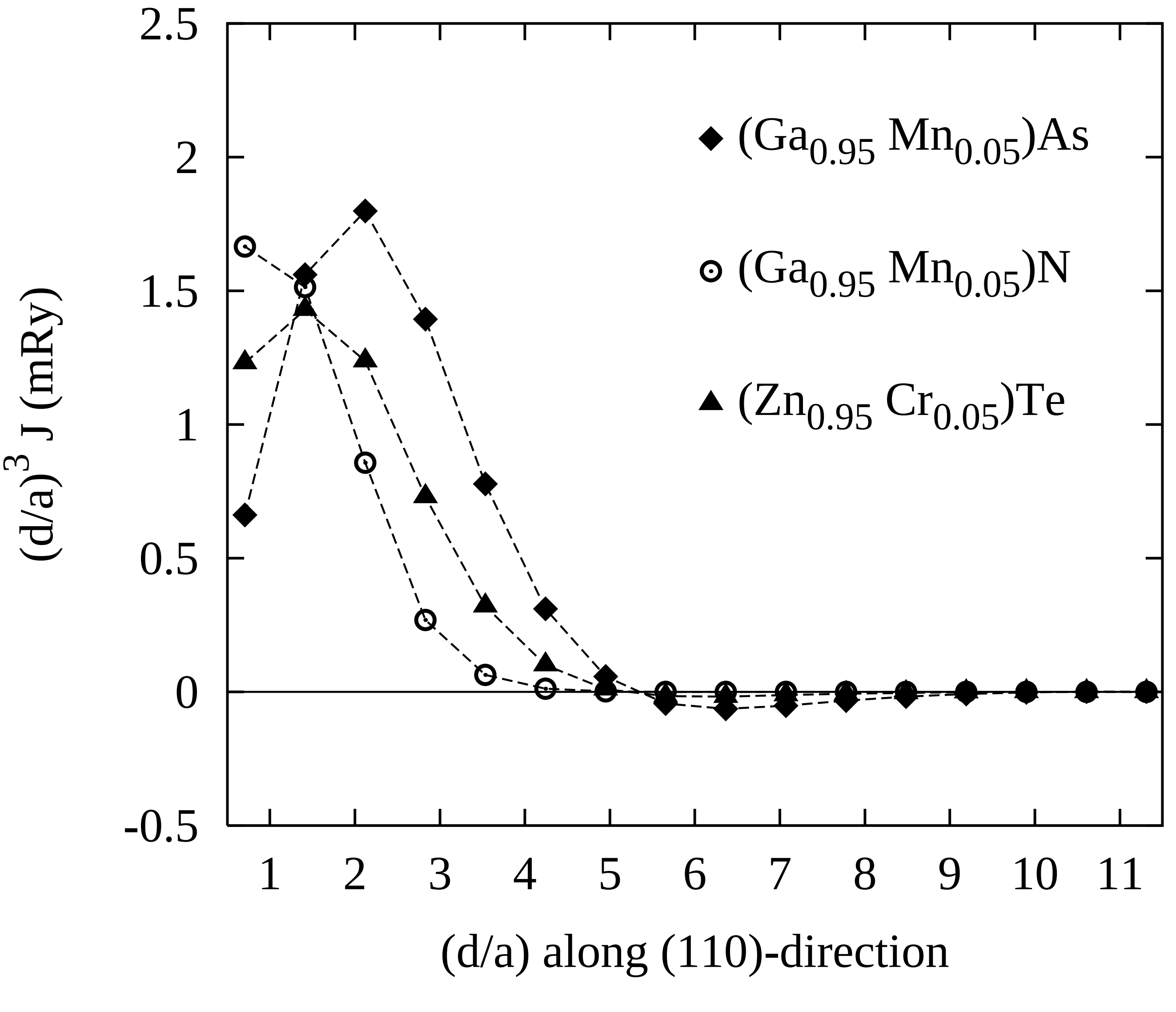
(multiplied by RKKY-factor $(d/a)^3$)



- [110]-direction **dominates**
- exchange interactions are **exponentially** damped due to alloy **disorder** and **halfmetallic** character
- exchange interactions are much more **localized** for Mn-doped GaAs as compared to Mn-doped GaN

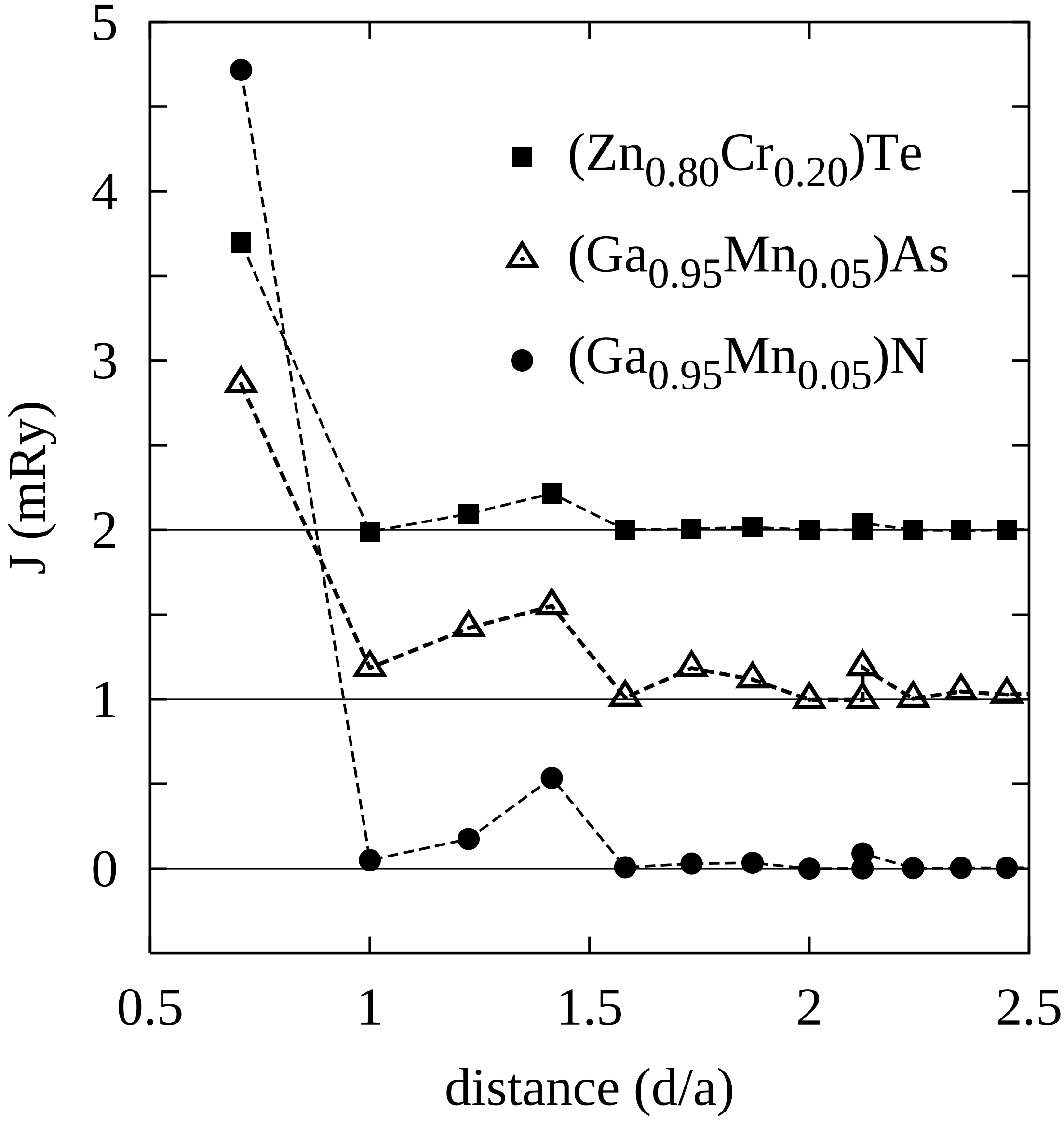
Exchange interactions along [110]-directions in various DMS alloys

(multiplied by RKKY-factor $(d/a)^3$)



- [110]-direction **dominates**
- exchange interactions are **exponentially** damped the **strongest (weakest)** damping is found in GaMnN (GaMnAs) alloys, ZnCrTe is intermediate

Exchange interactions in various DMS alloys

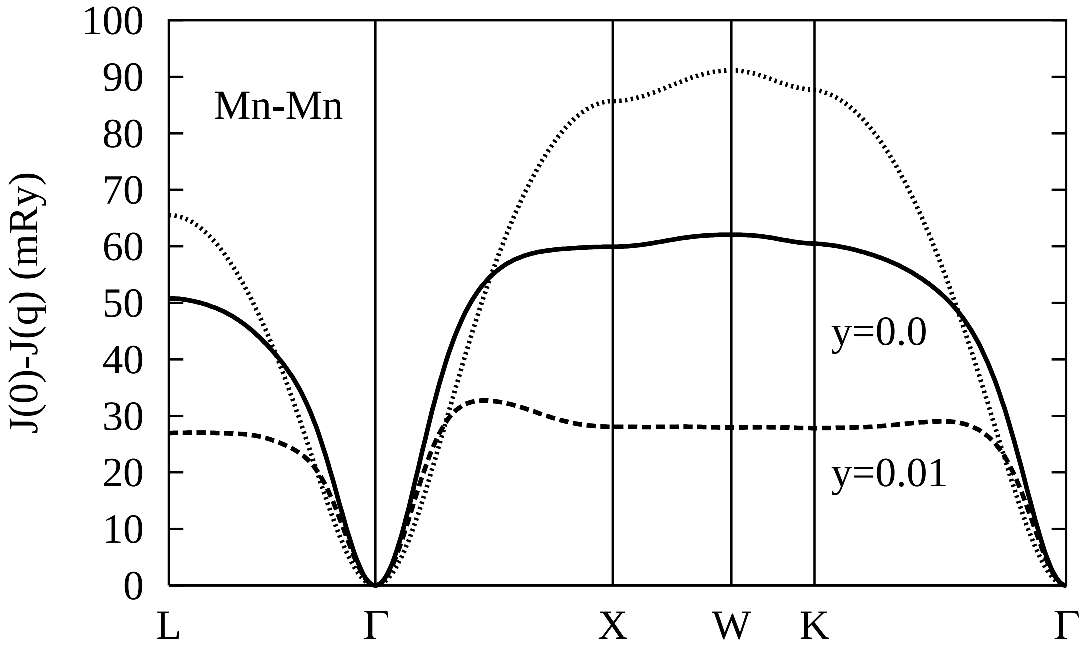


- exchange interactions in Mn-doped GAN **dominate**
- exchange interactions in Mn-doped GaAs are the most **extended**, those in GaMnN are the most **localized**

Lattice Fourier tranform $J(\mathbf{0}) - J(\mathbf{q})$, where

$$J(\mathbf{q}) = \sum_{i \neq 0} J_{0i} \cdot \exp(-i\mathbf{q} \cdot \mathbf{R}_i)$$

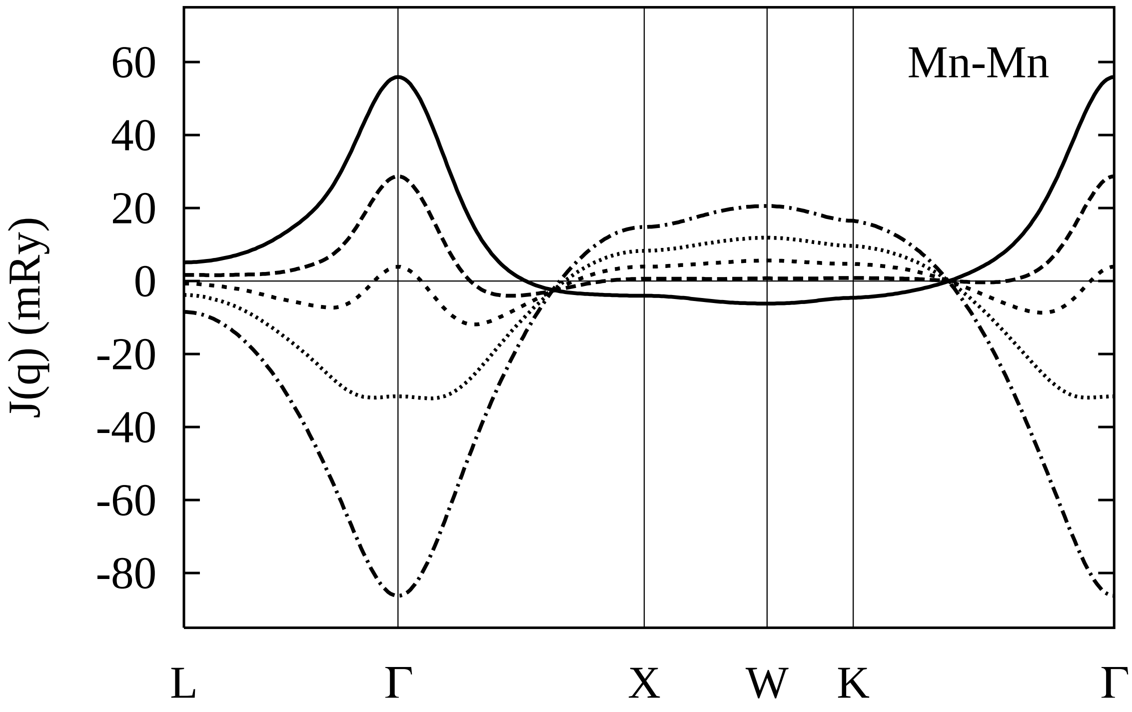
for $(\mathrm{Ga}_{0.94-y}\mathrm{Mn}_{0.05}\mathrm{As}_y)\mathrm{As}$ $(y = 0.0, 0.01)$ and $(\mathrm{Ga}_{0.95}\mathrm{Mn}_{0.05})\mathrm{N}$



- $J(\mathbf{0}) - J(\mathbf{q})$ is proportional to **magnon** dispersion law
- GaMnAs vs GaMnN: **flattness** of magnon dispersion law
  $\Rightarrow$ MFA and MC results are closer each other

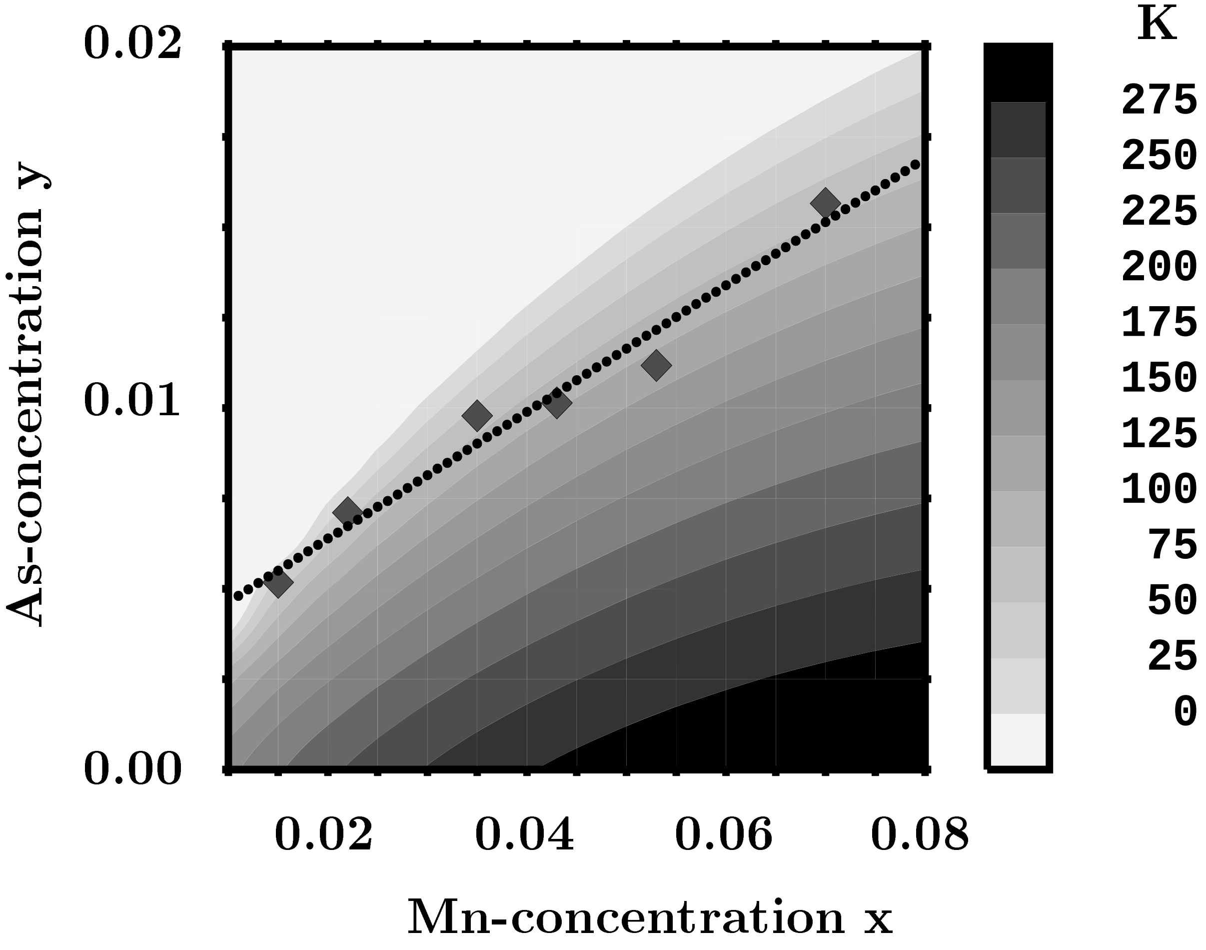
Phase-stability of $(Ga_{0.95-y}Mn_{0.05}As_y)As$ using the **lattice Fourier transform** $J(\mathbf{q})$, where

$$J(\mathbf{q}) = \sum_{i \neq 0} J_{0i} \cdot \exp(-i\mathbf{q} \cdot \mathbf{R}_i)$$



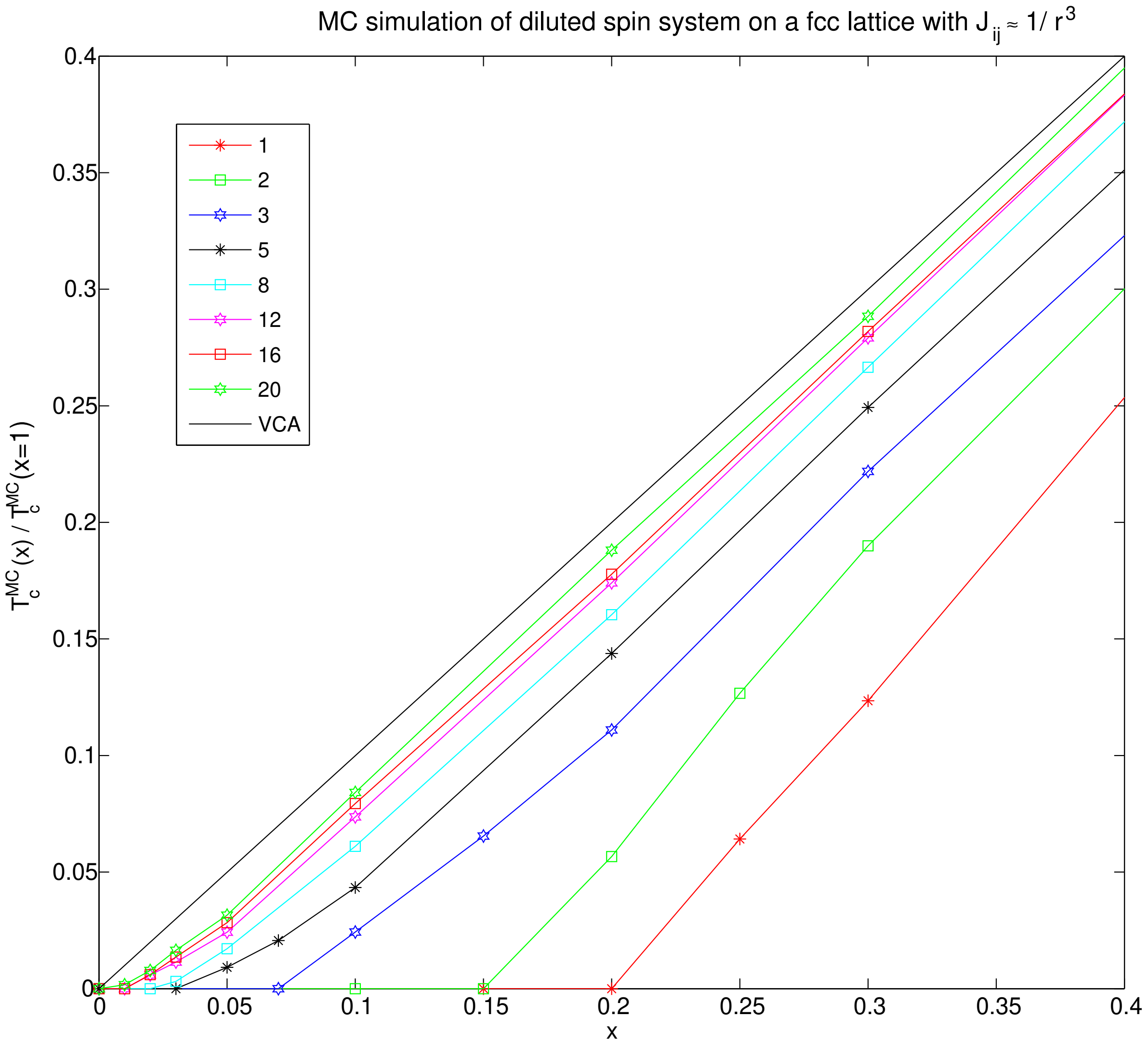
- **ferromagnet** is ground-state for **small y**
- the **stability** of the ferromagnetic phase **decreases** with **increasing compensation**
- the **flat part** in the **excitation** spectrum ⇒ the **MFA** is a good approximation for the **Curie temperature**

Concentration map of Curie temperatures of (Ga,Mn)As alloys in MFA:



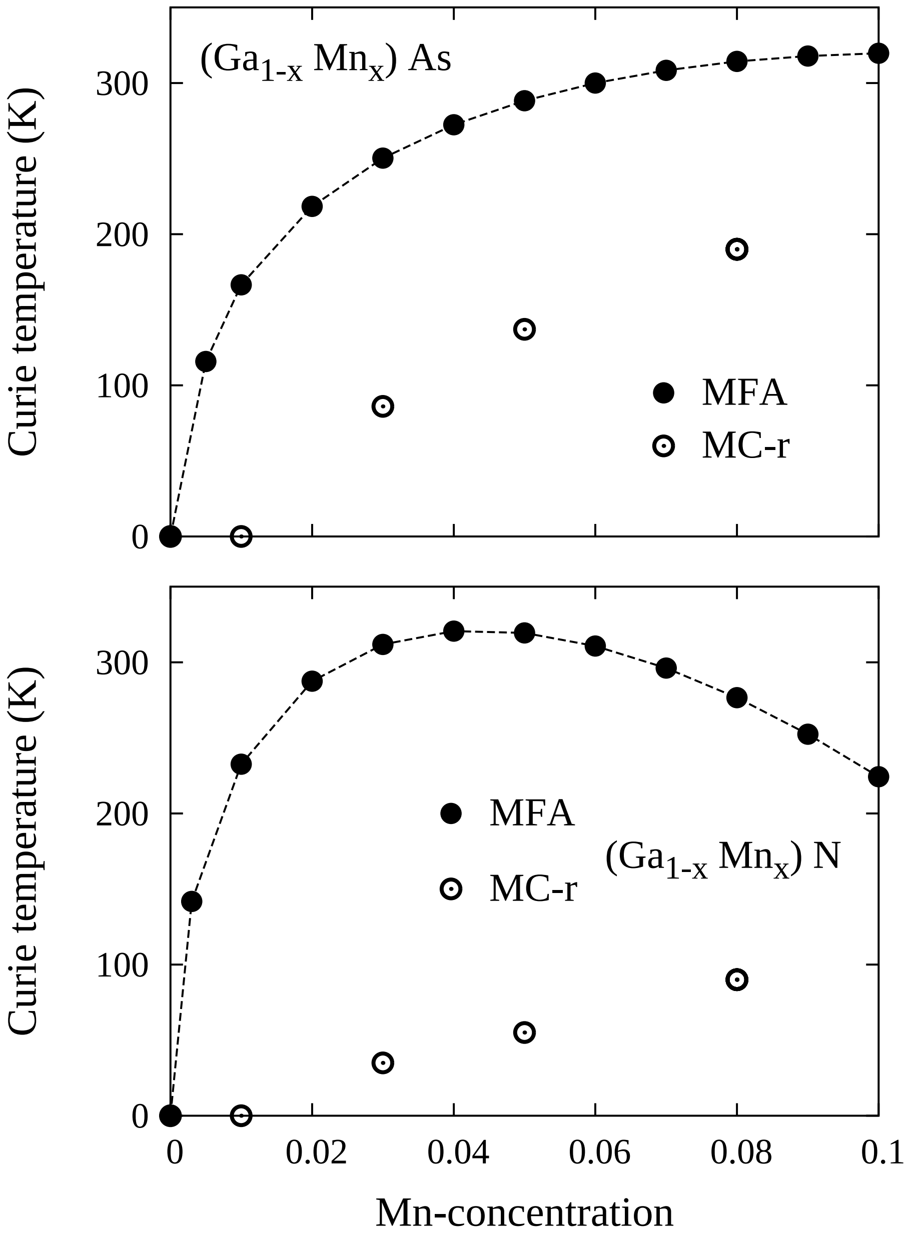
- **room** temperatures are reached **only** with **negligible** As-antisite content
- strong **reduction** of Curie temperature due to the presence of **compensating** As-antisite defects
- experimental data of Ohno et al. are **fitted** to MFA-results:
  $\Rightarrow$ the concentration of As-antisites **increases** with the concentration of Mn-atoms (samples are **compensated**)

Curie temperatures of fcc-random lattice (toy model): Mean-field vs Monte-Carlo (random lattice)



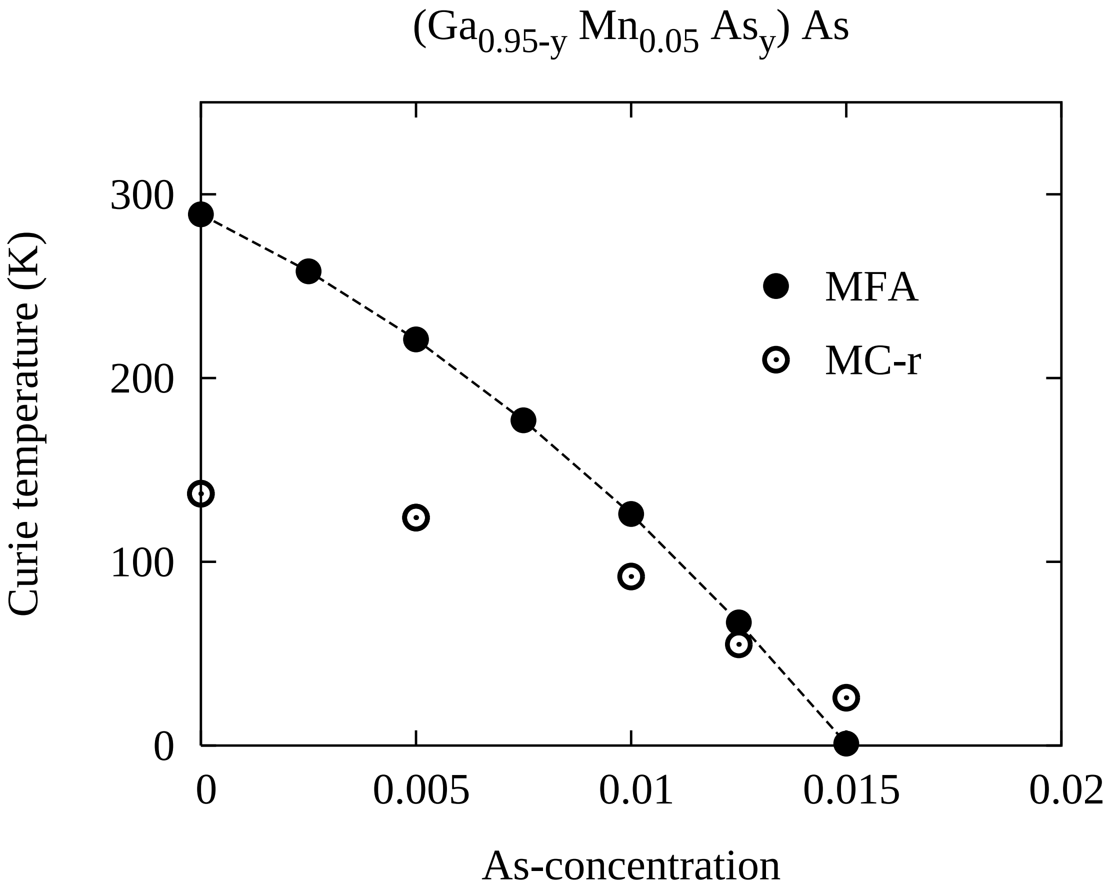
- fcc-random lattice: FM-interactions having RKKY-like decay with distance
- MFA-Curie temperatures are strongly **overestimated**, in particular for **short-ranged $\mathbf{J}_{ij}$** (case of DMS)
- MFA and MC-random agree reasonably for **long-ranged $\mathbf{J}_{ij}$**
- concentration gap for low x $\Rightarrow$ **magnetic percolation**

Curie temperatures of (Ga,Mn)As & (Ga,Mn)N alloys: Mean-field vs Monte-Carlo (random lattice)



- MFA-Curie temperatures are strongly **overestimated**, in particular for Mn-doped GaN alloys
- GaMnAs-MC: agreement with **experiment** (Edmonds *et al*)
- concentration gap for low x_{Mn} $\Rightarrow$ **magnetic percolation**

Curie temperatures of (Ga,Mn)As with As-antisites: Mean-field vs Monte-Carlo (random lattice)



- MFA and MC-random Curie temperatures **decrease** with **As-antisite** concentration (carrier-concentration effect)
- MC-random Curie temperatures decrease with $\mathbf{y}_{As}$ with much **smaller slope** as compared to MFA-temperatures
- ferromagnetism **disappears** for **larger** $\mathbf{y}_{As}$ in MC-random

Curie temperatures: $Zn_{1-x}Cr_xTe$ alloys

- **Various approximations for T_c**

Method	$Zn_{1-x}Cr_xTe$		
	x=0.05	**x=0.1**	**x=0.2**
experiment	–	–	**300** ±10
MFA-VCA	356 K	451 K	557 K
RPA-VCA	324 K	400 K	477 K
MC-VCA	315* K	410* K	491* K
MC-random	120* K	215* K	**301** K

* MC-calculations were performed for **smaller** simulation cells as compared to the case x=0.2

- VCA: the **averaged lattice** model was used to treat **disorder** in Heisenberg model while its **thermodymamics** was studied using the MFA, RPA, and the MC simulations

- Only the MC on the **random lattice** agrees with experiment, while the other approaches **strongly overestimate** the experimental Curie temperature

Curie temperatures: why the MFA fails?

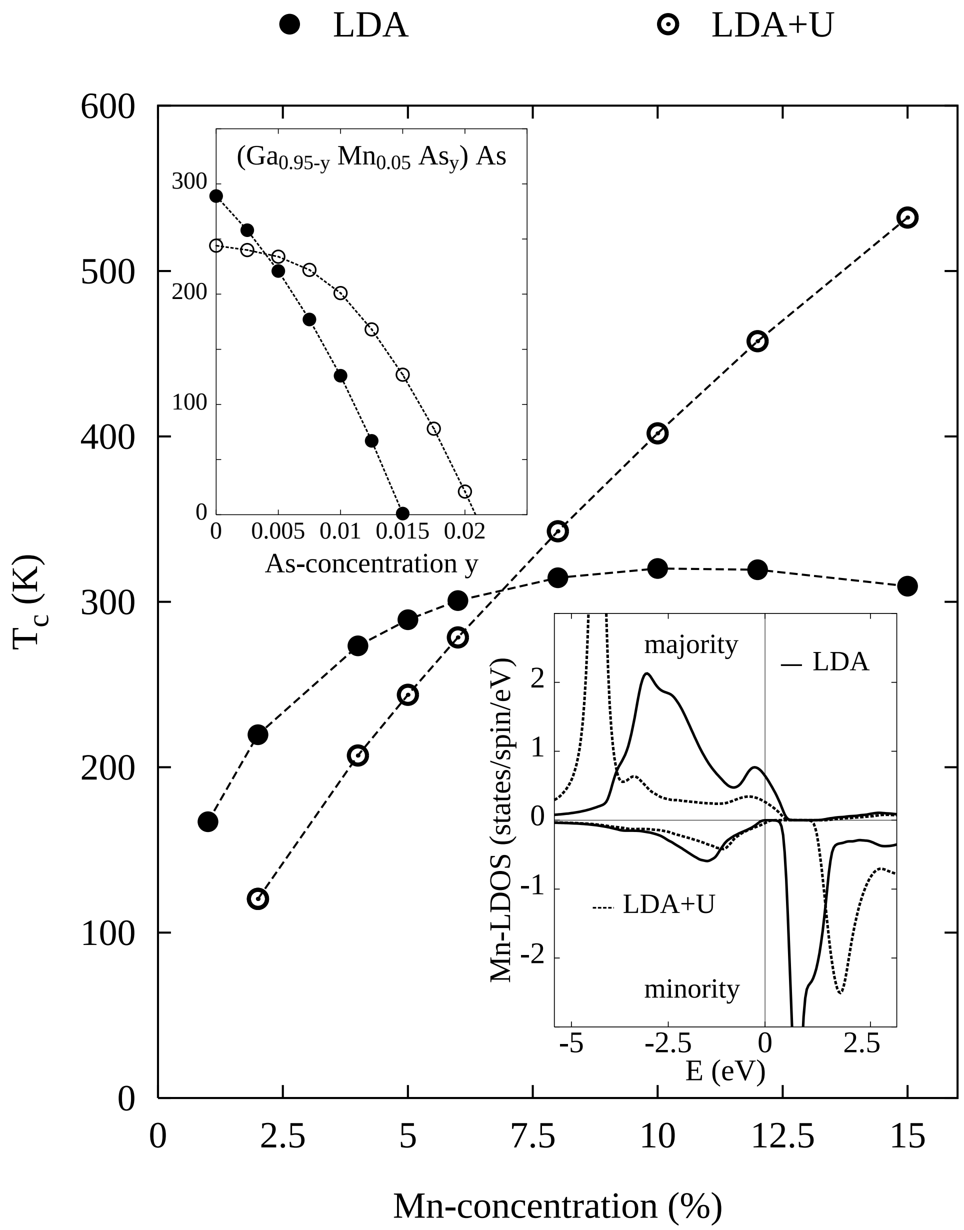
- MFA-VCA **overestimates** $T_c \Rightarrow$ the large 1st-NN exchange interactions are **incorrectly** treated in the framework of the VCA (strong disorder); $\Rightarrow$ **average distances** among magatoms are larger than 1st-NN distance for low concentration
- MFA-SC values are **smaller** than MFA-VCA for alloys with **large** 1st-NN exchange interactions (strong disorder) $\Rightarrow$ these values are **missing** in supercell approach (MFA-SC, low concentrations)

	approach			
Alloy	**VCA**	**SC***	**MC-R**	**exper**
$Ga_{0.95}Mn_{0.05}As$	287 K	245 K	**137** K	118 K
$Ga_{0.95}Mn_{0.05}N$	376 K	176 K	**55** K	–
$Zn_{0.8}Cr_{0.2}Te$	557 K	346 K	**301** K	300 ± 10 K

* Supercell magnon calculations (Sandratskii & Bruno), 16 (x=0.0625) and 4 (x=0.25) chemical units

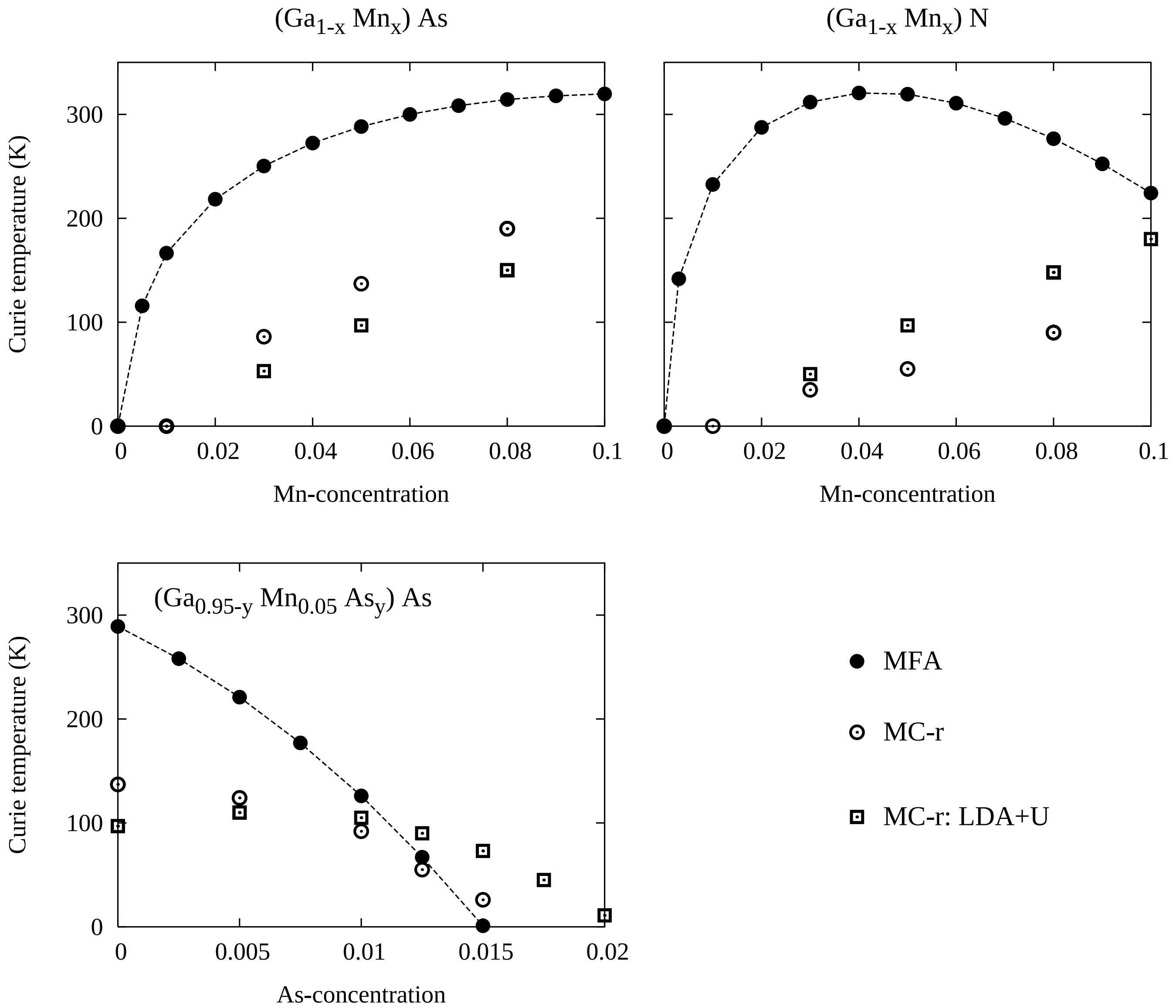
- MFA-VCA values are **close** to MC-R values if 1st NN are **reduced** (e.g. compensated GaMnAs with As-antisites)
- **Solution** $\Rightarrow$ **impoved** treatment of the **disorder** in exchange interactions e.g. via the **CPA** or via the **MC simulations** (exact, clustering effects)

Curie temperature of (Ga,Mn)As alloys in MFA: effect of electron correlations



- electron correlations **suppress** Mn-*d* character of impurity states at the Fermi energy and shift the center of the Mn-impurity bands **downwards**
- concentration-dependence of Curie temperature **changes** from **square-root** type behavior to an almost **linear**
- ferromagnetism **vanishes** for larger As-concentration in the LSDA+U as compared to LSDA

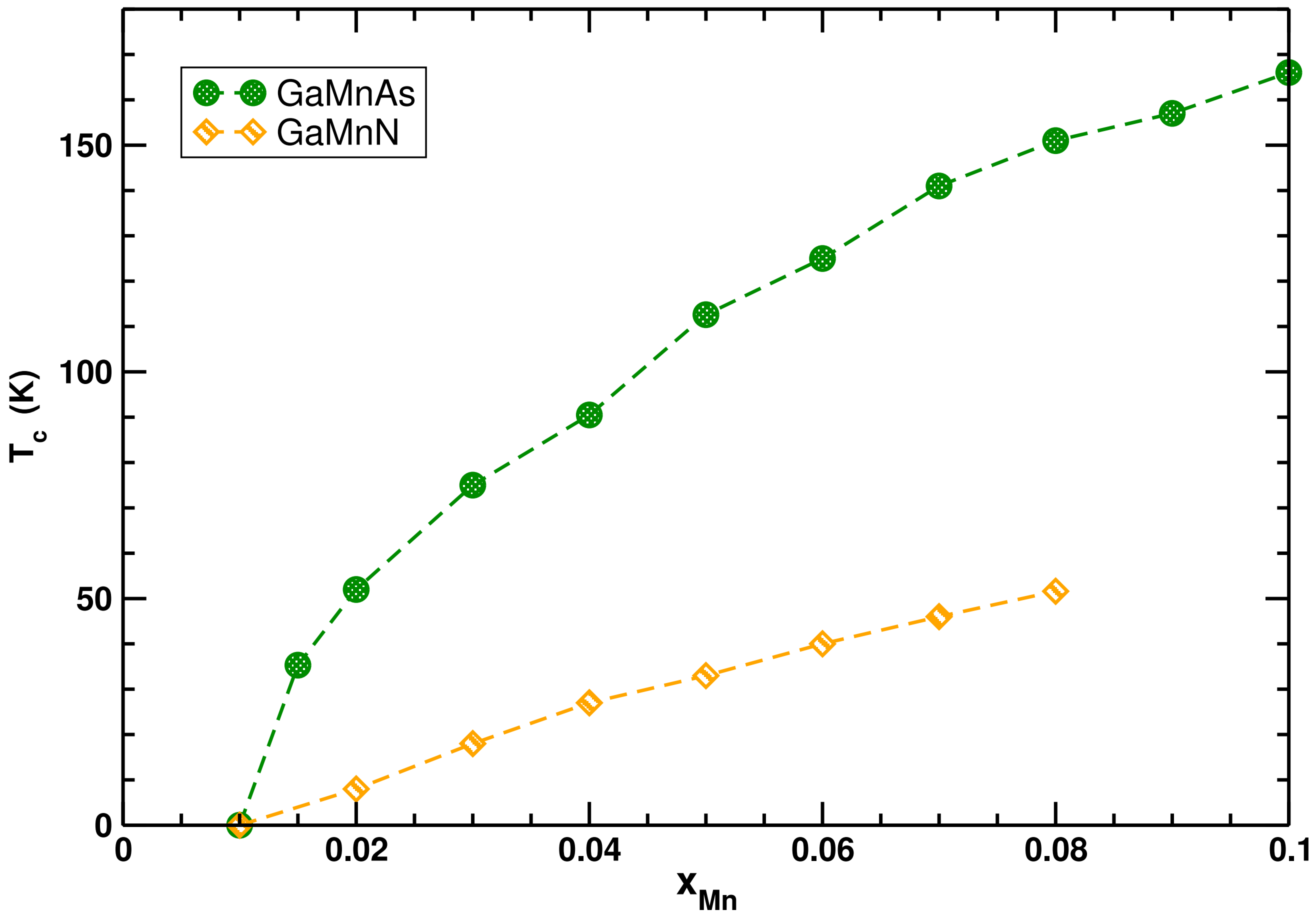
Curie temperature of (Ga,Mn)As/(Ga,Mn)N alloys: MC-random
combined effect of impurities and electron correlations



- results of MFA and MC-random are in qualitative **agreement**: Curie temperatures are **reduced (enhanced)** for (Ga,Mn)As ((Ga,Mn)N) alloys
- quantitative **differences** between LDA and LDA+U are **smaller** for MC-random as compared to MFA

Comparison of (Ga,Mn)As and (Ga,Mn)N: RPA-random

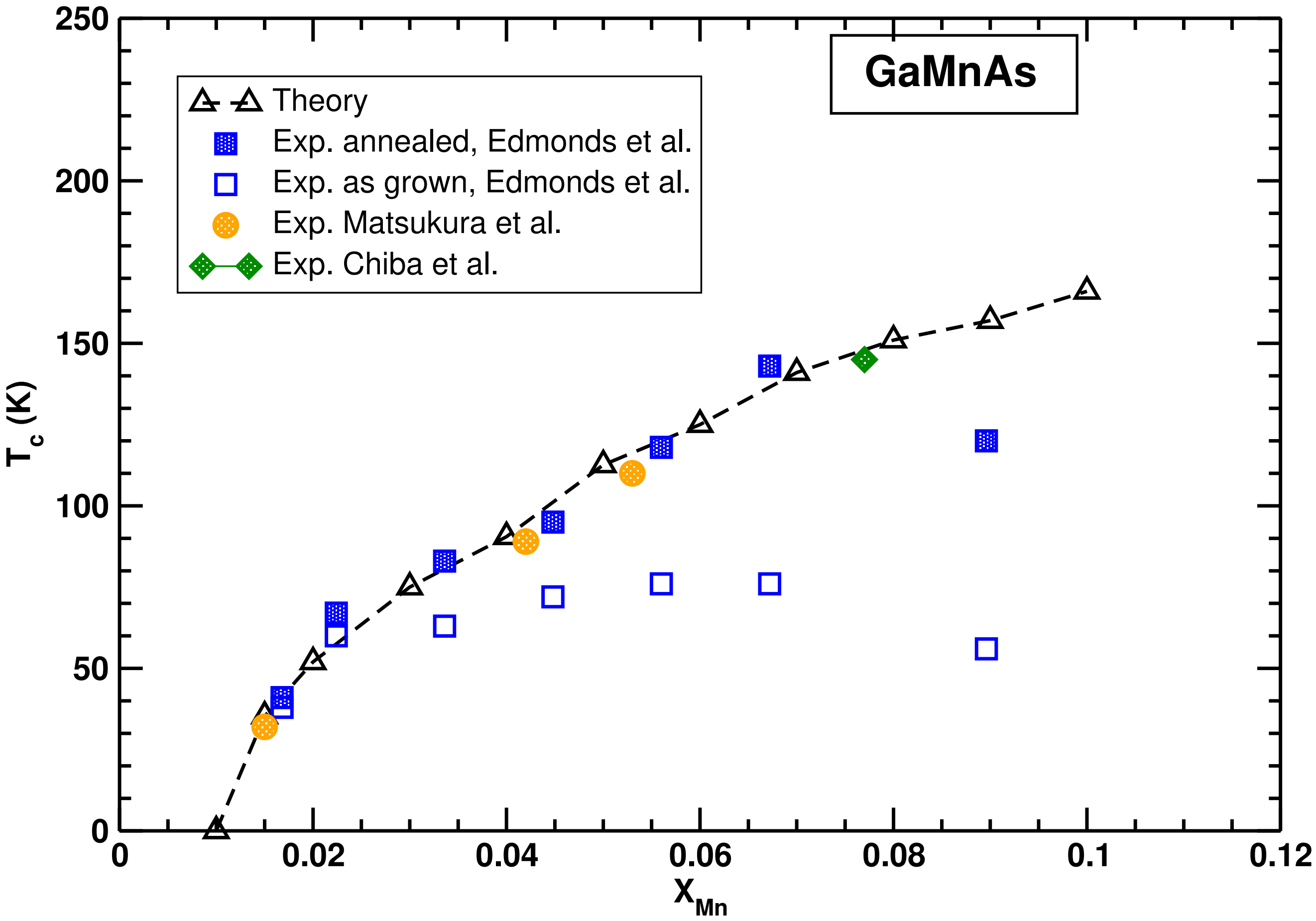
(Bouzerar *et al.*, 2004: cond-mat/0405322)



- Random **configurations** generated for Heisengerg model by the MC sampling
- RPA equations solved in **real space** for each configuration in the limit of **classical spins**
- **Selfconsistent** procedure and **RPA-estimate** of T_c are similar to that of H.B. Callen
- **Same** exchange interactions as for MC-random but **larger** number of **shells** can be used straightforwardly

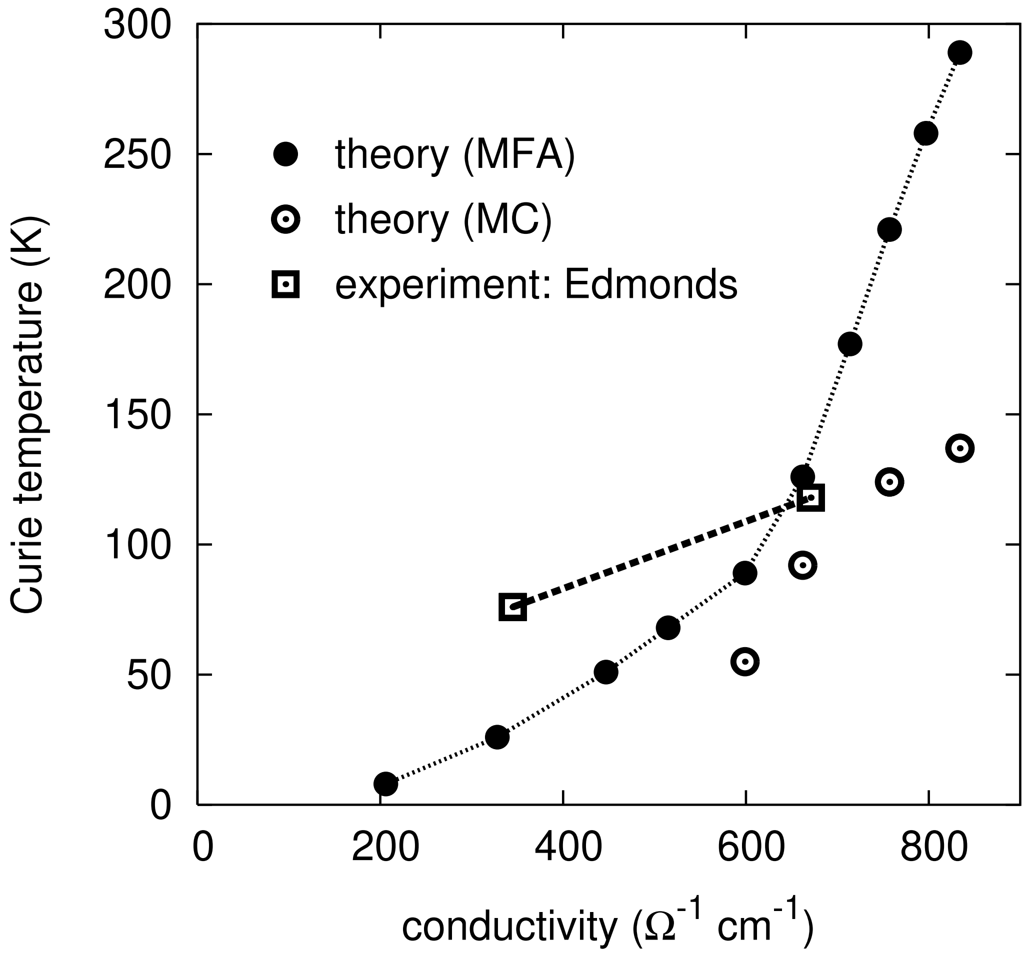
Curie temperature of (Ga,Mn)As: RPA-random (effect of randomness on the Curie temperature)

Bouzerar *et al.* 2004: cond-mat/0405322



- **Magnetic percolation** (concentration gap) for low Mn-concentration
- RPA-random results are in a good **agreement** with recent experimental data (Edmonds et al.) with a small amount of **compensating defects**
- A good **agreement** with recent MC-simulations (present, Sato *et al* (2004)

Correlation between Curie temperatures and conductivities in (Ga,Mn)As alloys:



- **Curie temperatures** and **conductivities** are calculated in the framework of the same **first-principles** alloy Hamiltonian, in which the **carrier lifetimes** due to disorder and the **carrier concentrations** are determined selfconsistently for a given alloy composition
- Both **exchange interactions** (mapping to Heisenberg model) and **conductivities** (Kubo-Greenwood approach with the vertex-corrections) depend on the **carrier concentration** and the **carrier lifetime** and are thus related each to other
- Theory **without adjustable parameters** and experiment for ($Ga_{0.95-y}Mn_{0.05}As_y$)As (both **as-grown** and **annealed** samples) agree reasonably well thus confirming the **carrier mediated** ferromagnetism in (Ga,Mn)As alloys