ELECTRONIC, MAGNETIC, AND TRANSPORT PROPERTIES OF COMPLEX MAGNETIC ALLOYS

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in collaboration with

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Motivation

Magnetic moments and Curie temperatures are the most important characteristics of the magnetic state. Their determinations from first-principles are of great importance for understanging of the origin of magnetism. This is in particular true for magnetic alloys.

A. Magnetic moments

- Elemental magnets and ordered magnetic alloys $\Rightarrow$ realiable determination of M_{tot} in the framework of the LSDA. In magnetic alloys in addition to M_{tot} exist also local magnetic moments on constituent atoms (problem: space partition between atoms)

- Random magnetic alloys represent much more involved problem, and some systems still represent challenge to solid state theory, e.g., DMS, random Heusler alloys, etc. The problem is typically solved using two possible approaches:

1. supercell approach $\Rightarrow$ very accurate LSDA methods are used but incorrect local environments (e.g. bcc-$A_{50}B_{50}$ vs CsCl $\Rightarrow$ SQS - artificial MLs with correct environment to first few NNs, numerically demanding, special concentrations only, damping due to alloy disorder is neglected

2. CPA $\Rightarrow$ reliable concentration trends, the effect of alloy disorder is included, less accurate LSDA methods are used which gives correct results for closed-packed lattices

B. Curie temperatures T_c

- Determination of T_c in the framework of the first-principle approach represents a big challenge to the solid state state theory, in particular for random magnetic alloys

- Two-step approach was succesfully used for elemental magnets and ordered magnetic alloys (e.g. Heusler alloys) and recently applied also to random alloys (DMS alloys in particular)

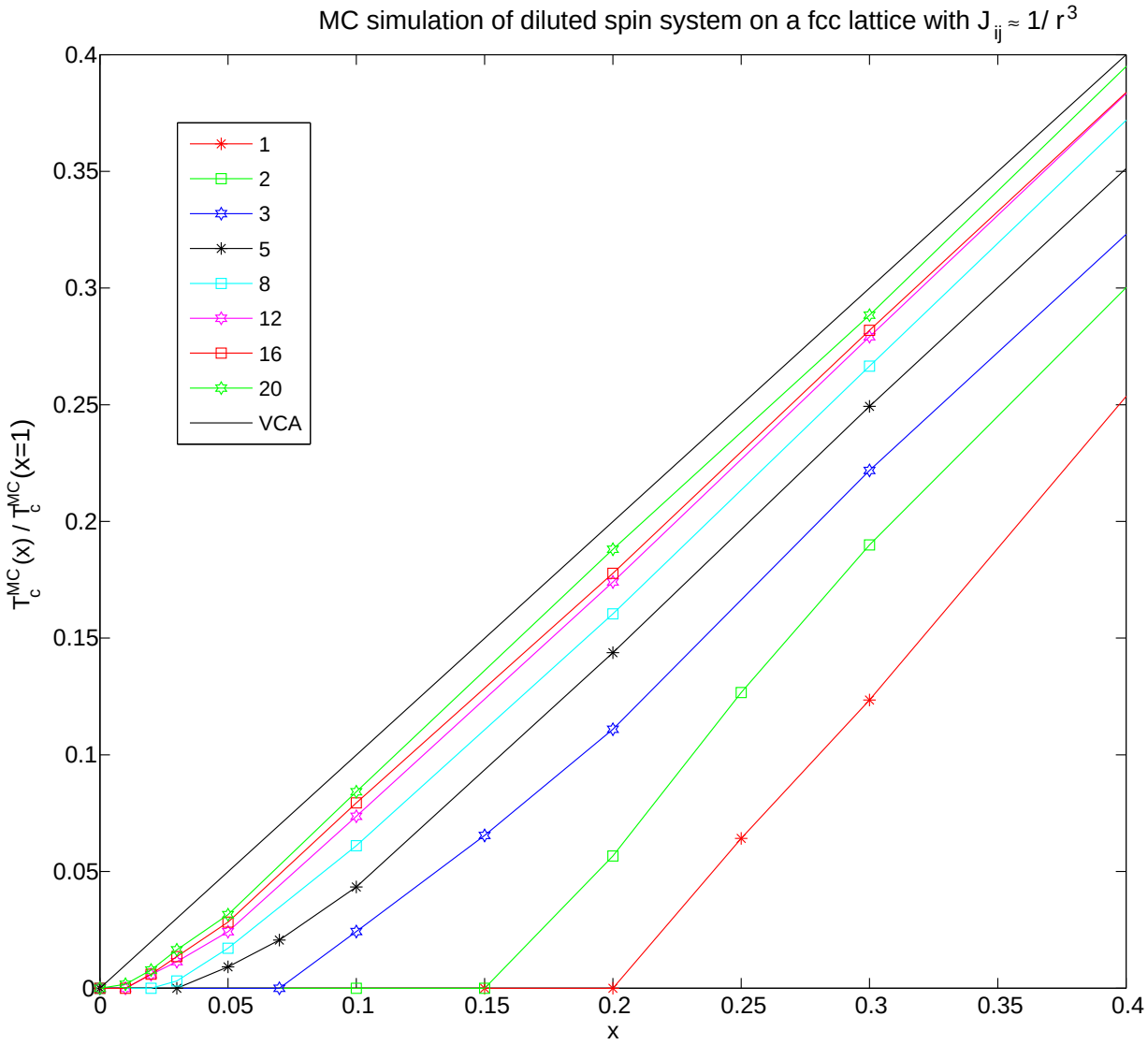
- 1st step: total LSDA energies of low-lying excitations (small spin-deviations from reference ferromagnetic state) are mapped onto the classical Heisenberg Hamiltonian (HH). During mapping pair-wise magnetic exchange interactions are obtained. For random alloys is generalization in the framework of the CPA more convenient and natural than supercell-approach (various concentrations, numerical feasibility). Local environment effects on magnetic interactions are, however, more naturally captured by supercell approach.

- 2nd step: Statistical study of HH $\Rightarrow$ classical HH properly includes transversal spin-fluctuations reducing the magnetization with temperature (contrary to the Stoner-excitation model!). Curie temperature (T_c) can be estimated in the framework of the MFA, RPA, and Monte-Carlo (MC) methods (RPA and MC gives usually similar T_c-estimates, MFA overestimate T_c).

- Two-step approach is well-justified for large rigid moments (Fe,Mn, ..) but it has limited validity for soft-magnetic moments like e.g. Ni. In the framework of the constrained LSDA theory was this limitation removed recently leading to the renormalized RPA approach (rRPA)

- Statistical treatment of random magnetic alloys may be quite difficult $\Rightarrow$ DMS alloys. The averaged lattice model (ALM) can be used (i) for concentrated alloys; (ii) if exchange interactions have spatially delocalized character; and (iii) magnetic moments are on both constituent atoms (the ALM fails e.g. in DMS alloys!).
  $\Rightarrow$ The problem of random alloys in the ALM is mapped into crystal-like case with effective exchange interactions (concentation weighted values of atom constituents in A_xB_{1-x} alloy): $x^2AA + 2x(1-x)AB + (1-x)^2BB$
  $\Rightarrow$ Indirect effect of disorder on perfect magnetic-sublattice: (Cu,Ni)MnSb alloy (Mn-sublattice is also 'crystal-like')

Magnetic percolation: toy model - MFA vs MC (Bergqvist)



- Some basic equations: classical Heisenberg Hamiltonian

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

Magnetic moments are included in the definition of J_{ij}^{eff} ($\mathbf{e}_i$ are thus spin-directions); $J_{ij}^{eff} > 0 / J_{ij}^{eff} > 0 \Rightarrow$ FM/AFM coupling

- Exchange interactions: magnetic alloy $\mathrm{A}_x\mathrm{B}_{1-x}$ (Q, Q'=A,B)

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

Δ_i^Q are exchange splittings on a given atom Q and $\bar{\mathbf{g}}_{i,j}^{Q'Q,\sigma}(z)$ propagates an electron of a given spin σ in random alloys between sites i, j occupied by atoms Q, Q'. Then

$$J_{ij}^{eff} = x^2\, J_{i,j}^{AA} + 2x(1-x)\, J_{i,j}^{AB} + (1-x)^2\, J_{i,j}^{BB}$$

- Curie temperature: various estimates

$$k_B\, T_c^{\mathrm{MFA}} = \frac{2}{3} J(\mathbf{0})\,, \quad \mathbf{J}(\mathbf{0}) = \mathbf{J}(\mathbf{q}) \;\; \text{for} \;\; \mathbf{q} = \mathbf{0}$$

Quantity $J(\mathbf{q})$ is the lattice Fourier tranform of real-space J_{ij}^{eff}

$$(k_B\, T_c^{\mathrm{RPA}})^{-1} = \frac{3}{2N} \sum_{\mathbf{q}} [J(\mathbf{0}) - \mathbf{J}(\mathbf{q})]^{-\mathbf{1}}$$

$$k_B\, T_c^{\,\mathrm{rRPA}} = k_B\, T_c^{\mathrm{RPA}} (1 - 6 \frac{k_B\, T_c^{\mathrm{RPA}}}{M\Delta})^{-1}$$

Remark 1: T_c^{RPA} is smaller than $\mathrm{T}_c^{\mathrm{MFA}}$

Remark 2: Constraining magnetic fields which appear as Lagrange multipliers in the constrained DFT are included in recent approach leading to renormalized J's/RPA (Bruno 2003)
$\Rightarrow$ rRPA enhances T_c as compared to conventional RPA

Computational tools

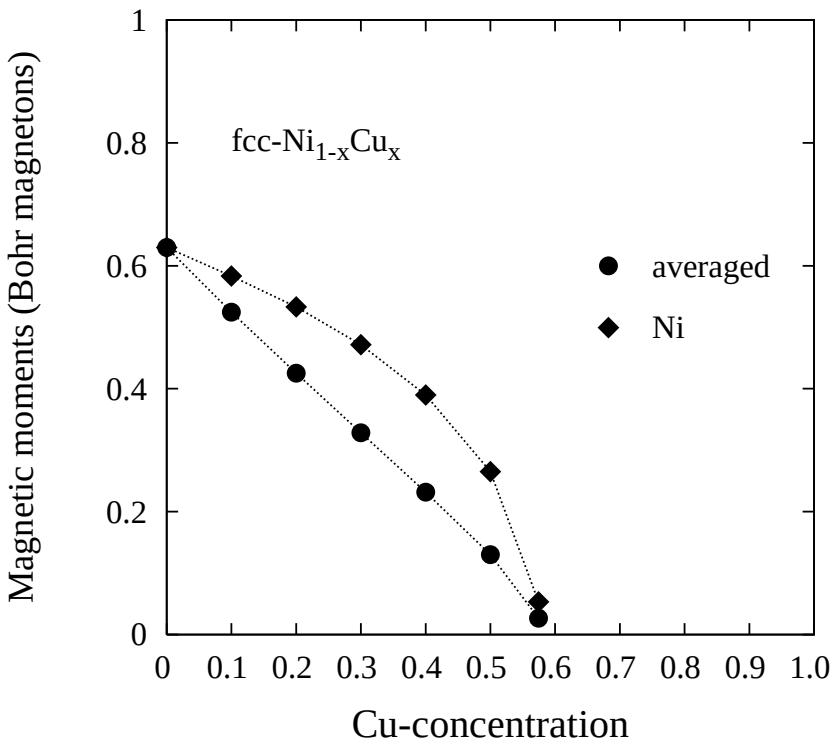
- Density functional theory (DFT) in the framework of local spin-density approximation: TB-LMTO method with chemical disorder described in the framework of the multi-sublattice CPA.

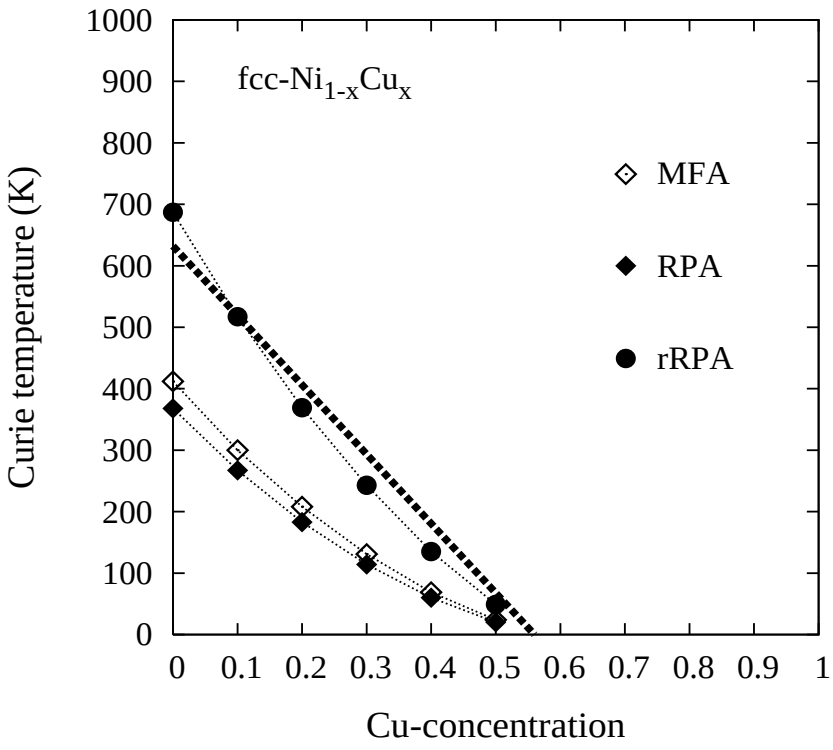
- Magnetic disorder or disorder is spin-orientations in fcc-NiMn/(Cu,Ni)MnSb alloys (Mn-atoms) $\Rightarrow$ included approximately in terms of the uncompensated DLM model $\Rightarrow$ 'random' alloy of Mn^{+} and Mn^{-} atoms in varying proportion of x^{+} and x^{-} ($x^{+}+x^{-}=1$) by using the CPA ($x^{+}=x^{-}=0.5$ is the DLM case)

- Two-step model generalized to random alloys with Curie temperatures estimated within the MFA, RPA, and rRPA in the framework of the ALM model.

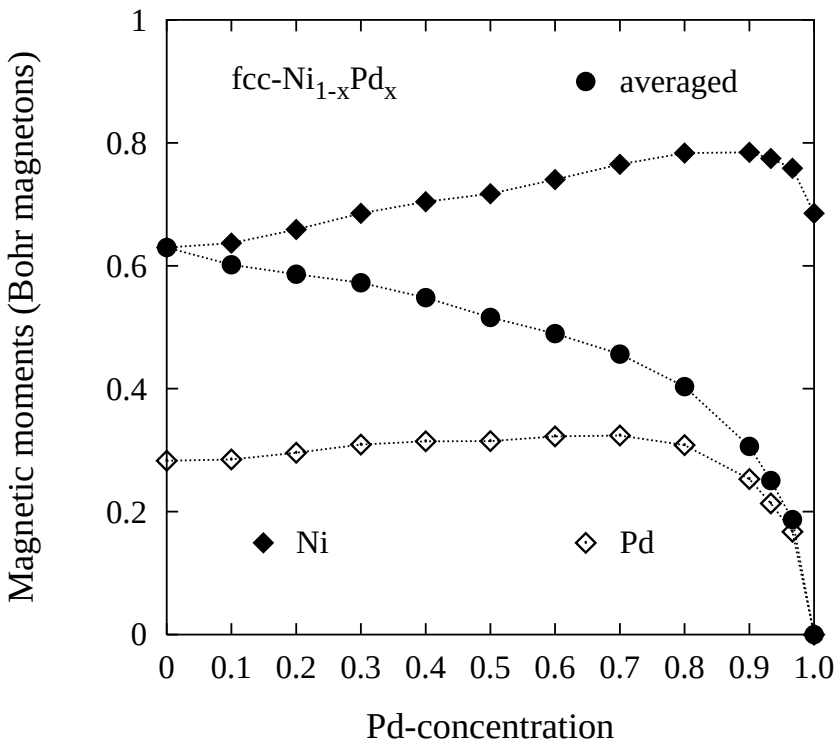
Our aim and motivation: Ni-based alloys

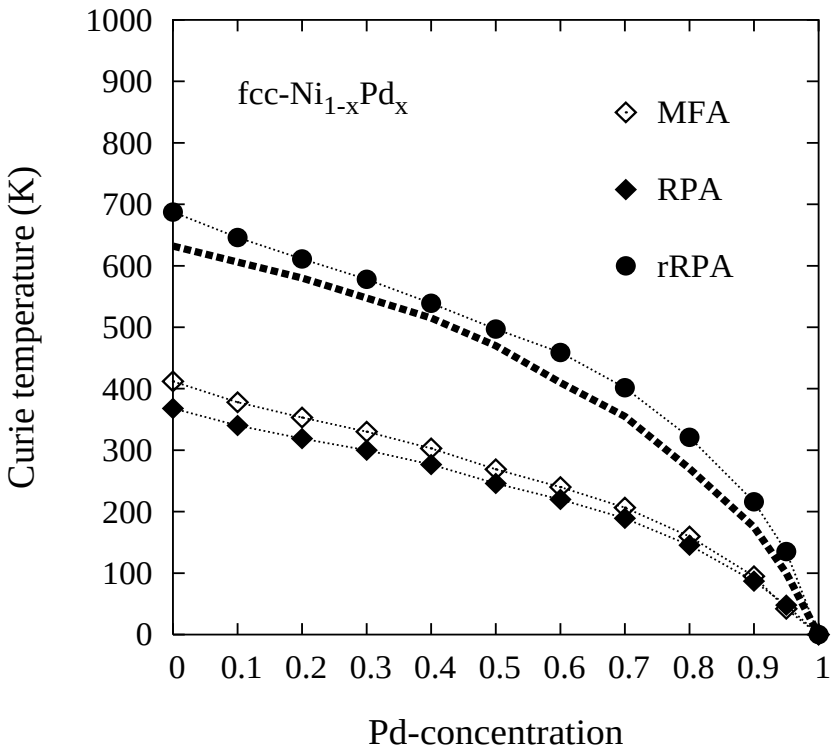
Determination of concentration trends of magnetic moments and Curie temperatures for fcc-NiCu, fcc-NiPd, fcc-NiFe, fcc-NiMn, and fcc-NiCo magnetic alloys and comparison with experiment





- Random fcc-$Ni_{1-x}Cu_x$ alloys (only one atom is magnetic)
- Linear decrease of $M^{Ni} \Rightarrow$ textbook example but in fact a delicate balance of sp-d charge transfer (M^{Cu} is almost zero)
- Very good agreement of T_c for the rRPA model





- Random fcc-$Ni_{1-x}Pd_x$ alloys (Pd is hihgly polarizable)
- M^{Ni} increases with Pd-content while M^{Pd} varies only weakly and collaps for x_{Pd} close to 1.
- Very good agreement of T_c for the rRPA model

Effect of structure on magnetic moment and T_c: fcc- vs bcc-Permalloy (PY: x_{Fe}=0.25)

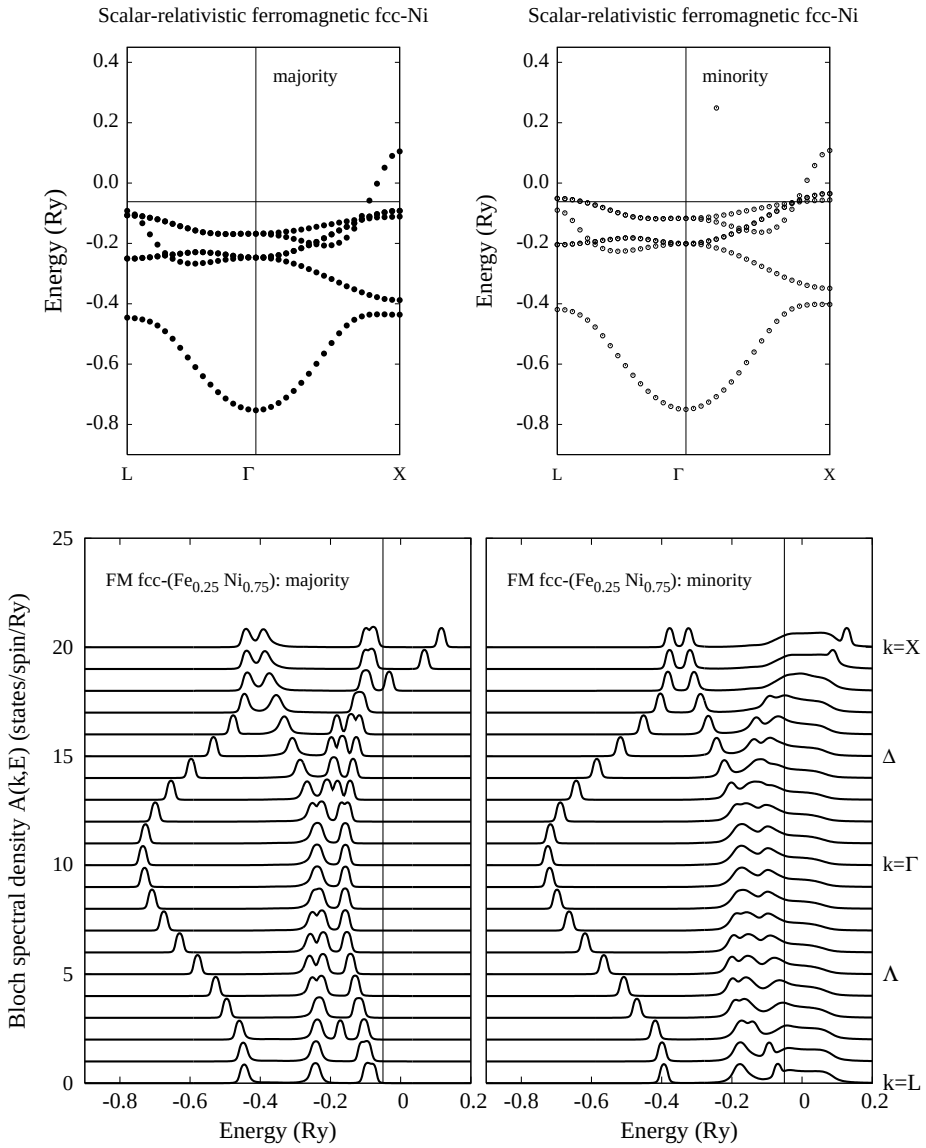
- Triple wedge MBE-technology ⇒ GaAs|bcc-PY and GaAs|Au|fcc-PY are grown up to 20-25 MLs (scaling extrapolation of T_c to infinite samples)

- Experiment: fcc/bcc-PY ⇒ M_{tot}=1.07/1.03 μ_B
  Theory: fcc/bcc-PY ⇒ M_{tot}=1.12/1.09 μ_B

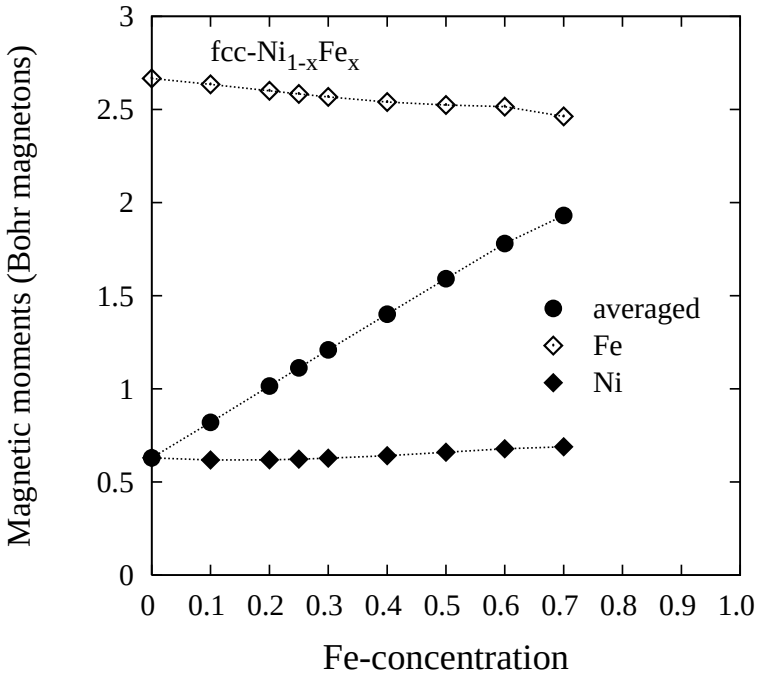
fcc-/bcc-Permalloy: Curie temperatures

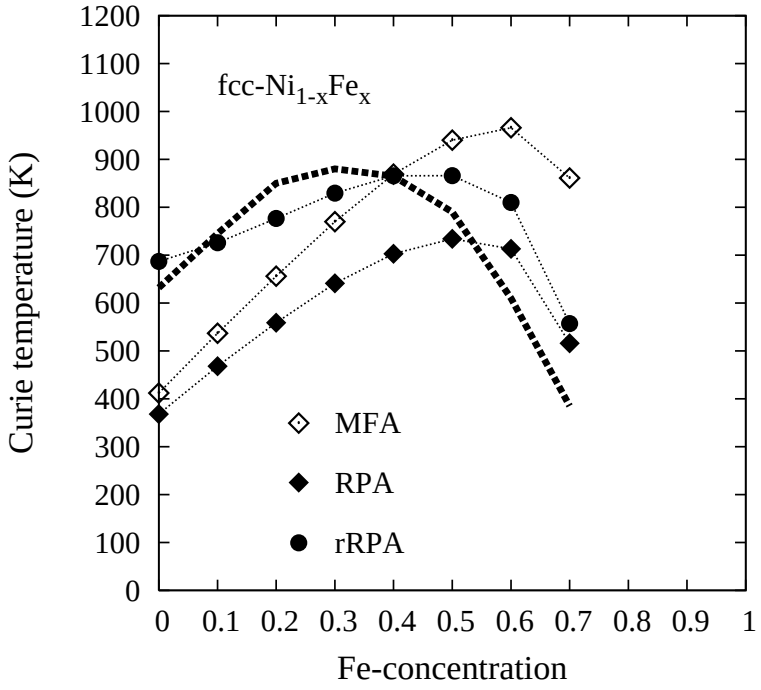
system	T_c^{MFA}	T_c^{RPA}	T_c^{rRPA}	T_c^{exp}
bcc Py	605	466	586	553
fcc Py	723	608	812	871 (858)

- The renormalized RPA gives best agreement with experiment
- $T_c^{bcc} < T_c^{fcc}$ ⇒ lower coordination of bcc-lattice while exchange integrals are comparable for fcc-/bcc-lattices

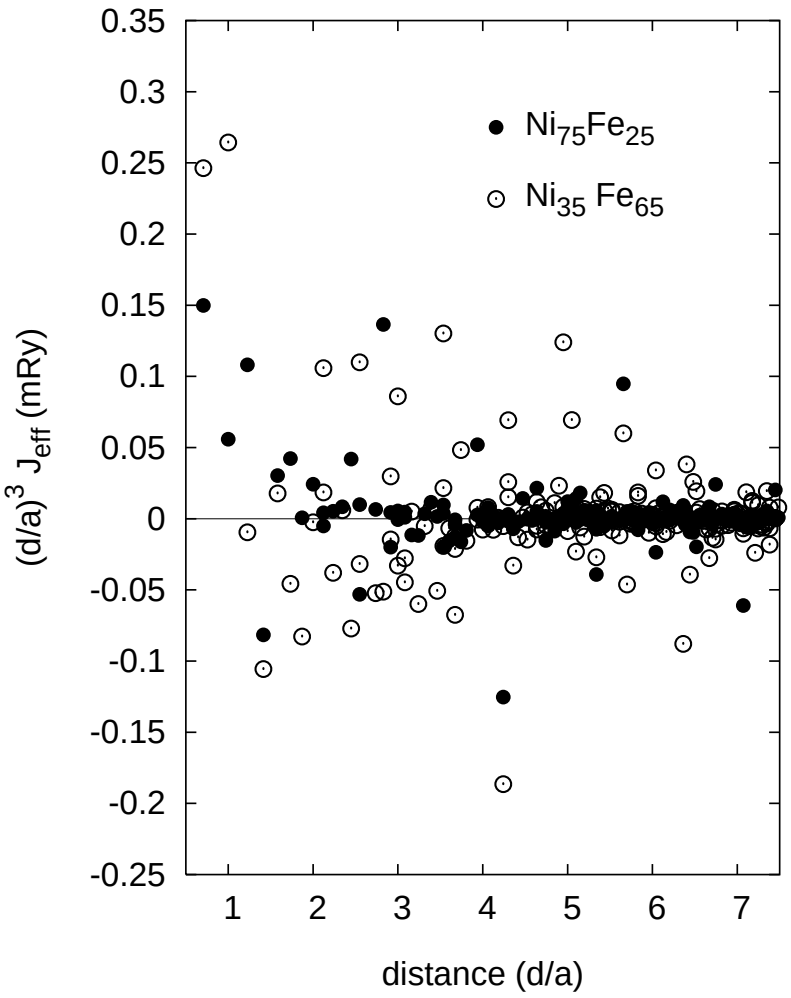


- Bloch spectral functions for PY=fcc-$Ni_{0.75}Fe_{0.25}$ alloys: different influence of disorder on maj/min states

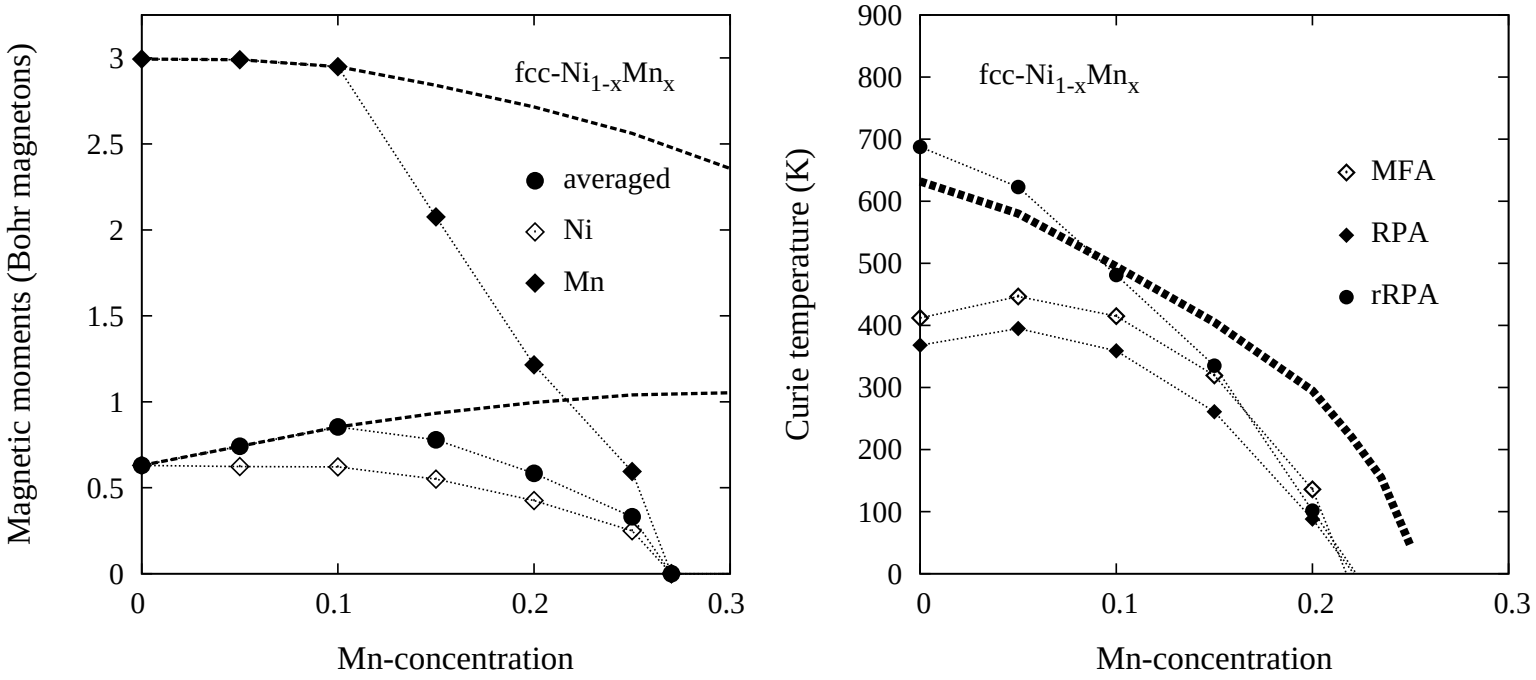




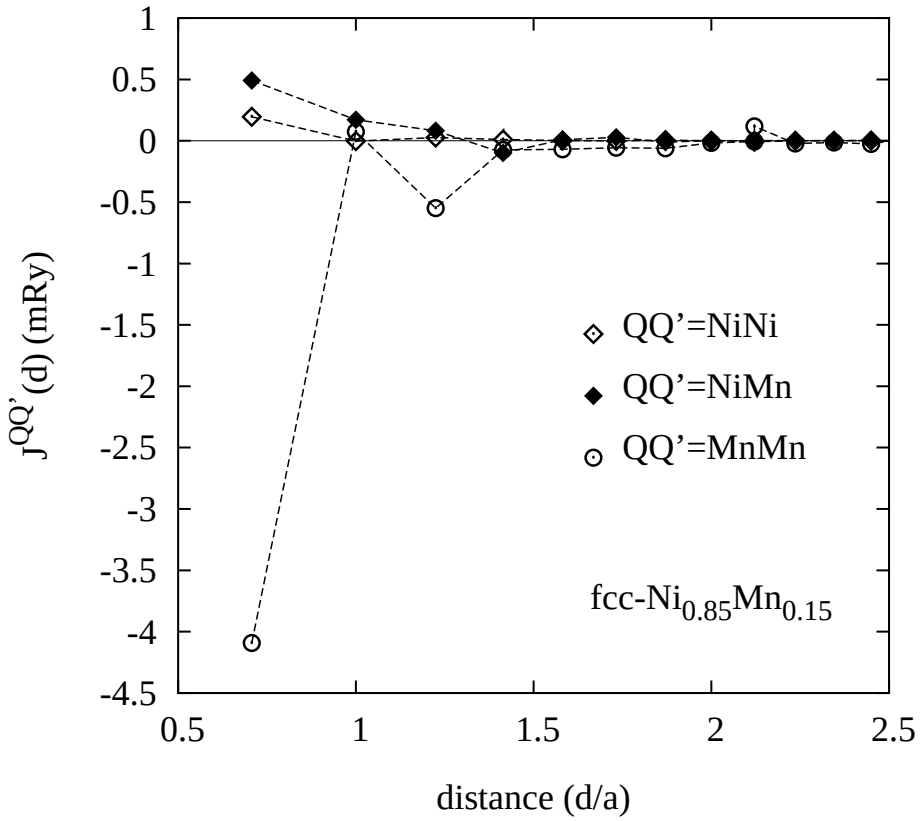
- Random fcc-$Ni_{1-x}Fe_x$ alloys: M^{Ni} and M^{Fe} varies weakly with Fe-content $\Rightarrow$ linear increase of M_{tot} with x_{Fe}
- Dramatic concentration dependence of T_c unexpected from the linear dependence of M_{tot} on composition
  $\Rightarrow$ pronounced maximum for $T_c = f(x_{Fe})$
- Reasonable agreement of T_c for the rRPA model with a shift of T_c-maximum to higher x_{Fe}



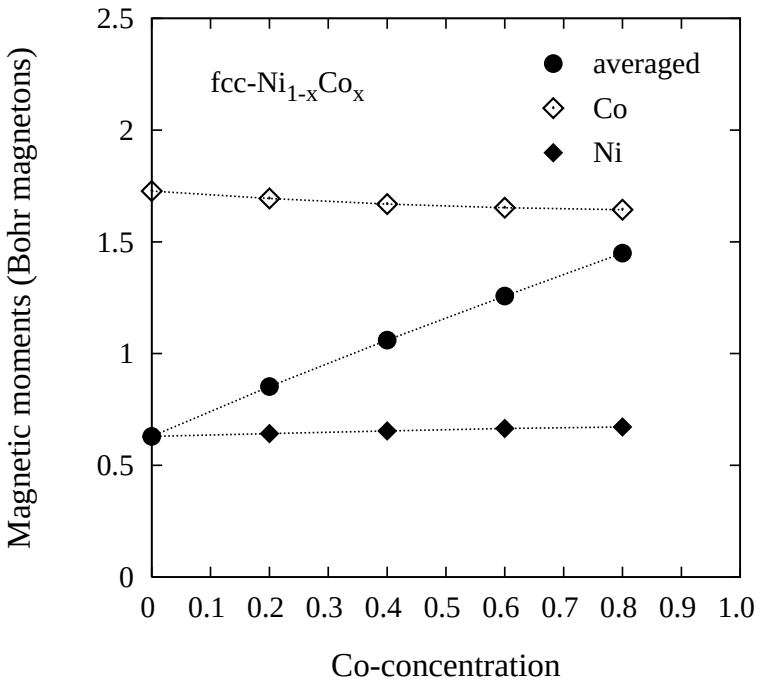
- Random fcc-$Ni_{1-x}Fe_x$ alloys: $J^{\rm eff}$'s increase with $x_{\rm Fe}$ but the frustration (antiferromagnetic interactions) increase strongly for larger $x_{\rm Fe} \Rightarrow T_c$ maximum

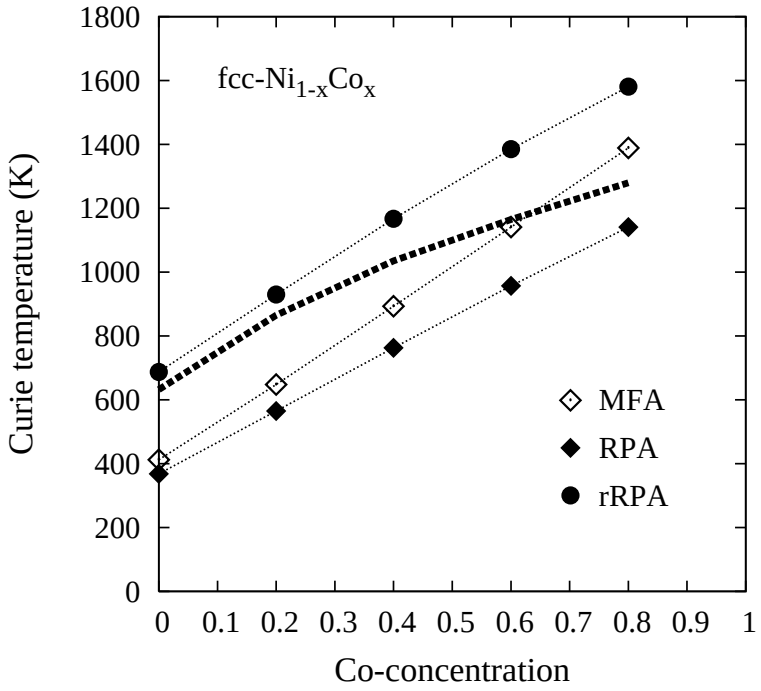


- Random fcc-$Ni_{1-x}Mn_x$ alloys: ferromagnetic description fails to reproduce M_{tot} and M^{Mn} concentration dependence
- Uncompensated DLM model explains experiment succesfully: $\Rightarrow$ x^+:x^- ratio for each x_{Mn} was determined selfconsistently from the total-energy minimization
- A good agreement of T_c for the rRPA model with a shift of magnetism extinction to a slightly lower x_{Mn}.



- Random fcc-$Ni_{1-x}Mn_x$ alloys: decrease of the Curie temperature with Mn-content is due to dominating negative Mn-Mn exchange interactions. Exchange interactions were obtained from the reference ferromagnetic state even for concentrations where uDLM is the ground state (rigidity of Mn-moments)





- Random fcc-$Ni_{1-x}Co_x$ alloys: M^{Ni} and M^{Mn} are almost concentration independent $\Rightarrow$ linear dependence of M_{tot} on composition
- A good agreement of calculated T_c for the rRPA model with experiment only for Ni-rich alloys $\Rightarrow$ an improvement can be obtained by including electronic entropy for larger Co-content but in general Co-represents a problem for the theory

Conclusions: Ni-based TM-alloys

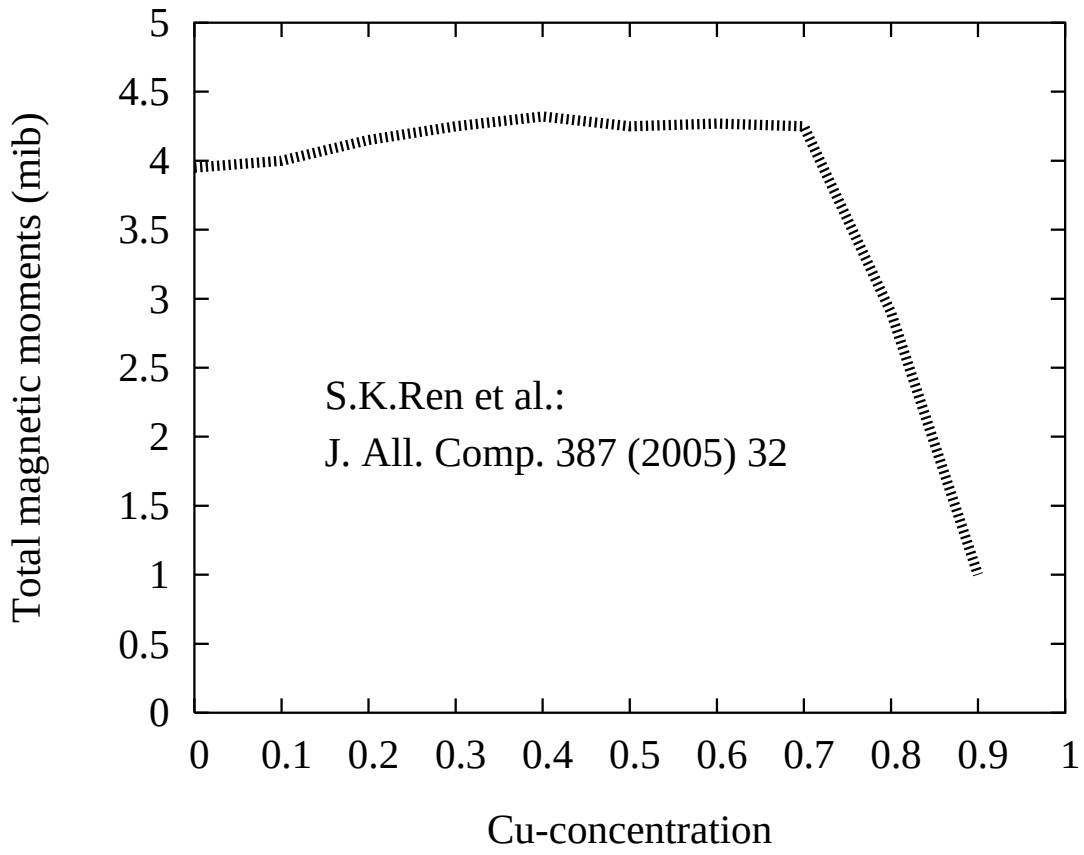
- First-principles study of magnetic and thermodynamical properties of a broad range of Ni-based fcc-ferromagnetic alloys including NiCu, NiPd, NiFe, NiMn, and NiCo systems over the whole concentration range.
- There is very good agreement of calculated M_{tot} (and of component magnetic moments if available) with experiment.
- Only uncompensated DLM model (and not the ferromagnetic one) describe properly behavior of fcc-NiMn alloys
- Only the renormalized RPA approach decribe reasonable well the concentration dependence of the Curie temperature while the MFA/RPA are in much worse quantitative agreement with the experiment. The agreement between theory and experiment is worse in Co-rich NiCo alloy.
- Exchange interactions allows to understand a complex behavior of T_c=f(x_Q), Q=Fe,Mn random magnetic alloys

Our aim and motivation: (Cu,Ni)MnSb alloys

Theoretical study of properties of semiHeusler (Cu,Ni)MnSb alloys from first-principles ⇒ Heusler alloys are promissing materials for spintronics and represent also interesting physics (non-stoichiometric alloys: magnetocalometric effect (NiMnSn))

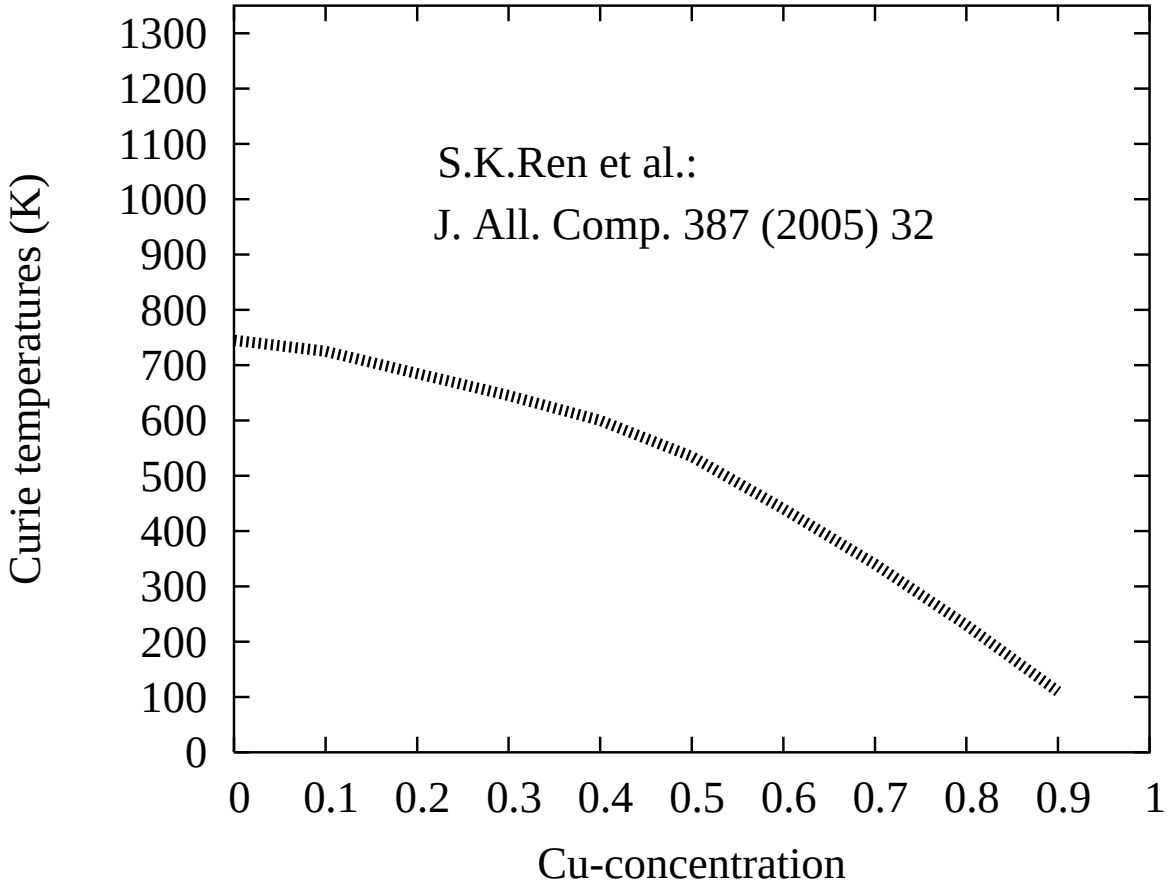
- structurally are compatible with semiconductors: 4 fcc lattices along [111] ⇒ (Cu,Ni)-Mn-I-Sb vs Ga-As-I1-I2
- Curie temperature can be well above room T
- reliable experiments can also serve as suitable tests for more complex systems (e.g. diluted magnetic semiconductors), in particular for *ab-initio* approaches
- complex study comprising electronic, magnetic, thermodynamic (Curie T), and transport properties using a unified first-principles approach ⇒ predictive power
- a possibility to study the effect of substitutional (Cu-Ni) and magnetic disorders (NiMnSb - FM, CuMnSb - AFM)
- possible effect of electron correlations in narrow Mn-bands

Experiment: Concentration dependence of magnetic moments in (Cu,Ni)MnSb alloys



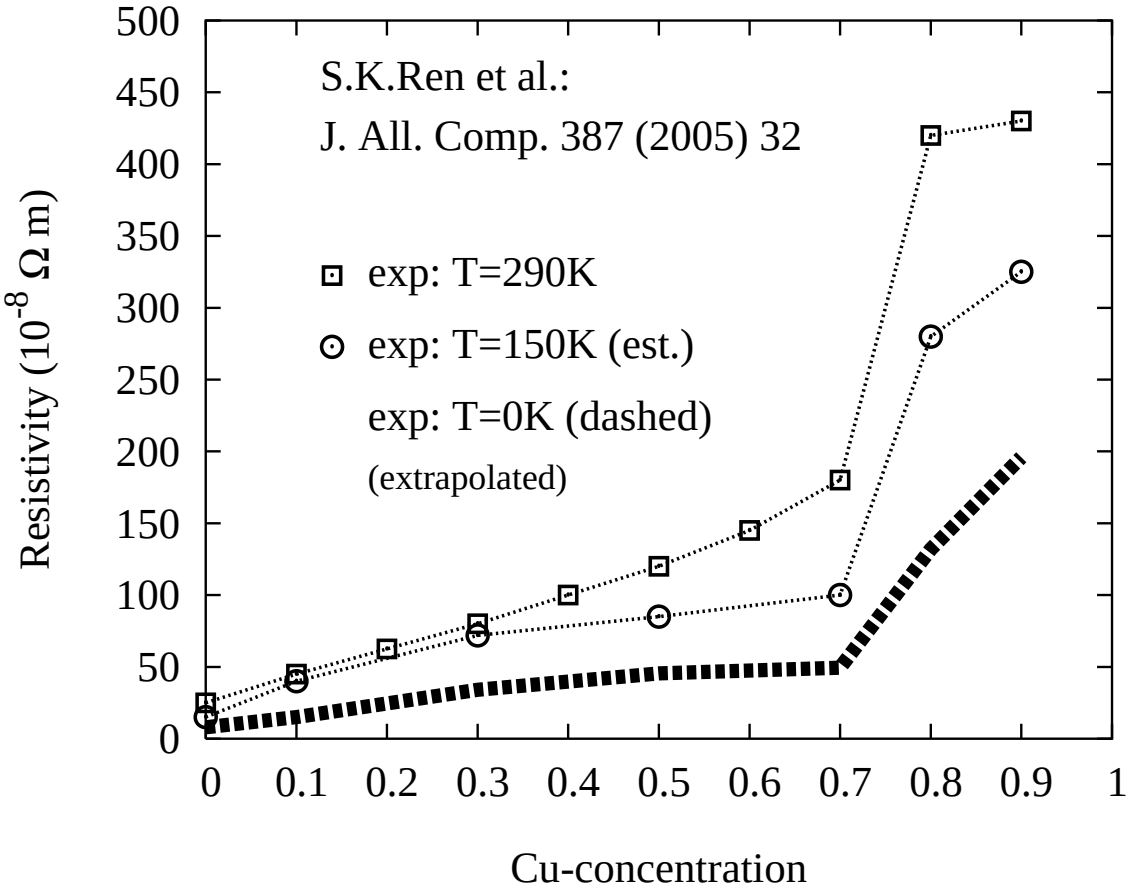
- Abrupt change of M=f(x_{Cu}) dependence at $x_{Cu} \approx 0.7$
- A weak M=f(x_{Cu}) dependence of M for $x_{Cu} \leq 0.7$

Experiment: Concentration dependence of Curie T of (Cu,Ni)MnSb alloys



Smooth $T_c = f(x_{Cu})$ dependence

Experiment: Concentration dependence of resistivity of (Cu,Ni)MnSb alloys



- Abrupt change of ρ=f(x_{Cu}) dependence at about $x_{Cu} \approx 0.7$
- Strong T-dependence of resistivity

A simple qualitative explanation of experiment

- NiMnSb is the ferromagnet, CuMnSb is the antiferromagnet
- Phase transition ferromagnet $\Rightarrow$ antiferromagnet starts at certain x_{Cu} and leads to magnetic disorder (disorder in spin-orientations) on structurally non-random Mn-sublattice
- Magnetic disorder leads to an abrupt reduction of magnetization and to an abrupt increase of residual resistivity as compared to the reference ferromagnetic state
- Pair exchange interactions for large rigid magnetic moments like those on Mn-sites are only weakly influenced by magnetic disorder $\Rightarrow$ smooth concentration dependence of T_c

Our aim

A quantitative explanation of experiment in the framework of parameter-free theory based on DFT-formalism

Conductivity: residual resistivity

Ab initio theory of residual resistivity is based on two steps:

- Selfconsistent electronic structure within the LSDA-CPA: the same as that used for mapping to the Heisenberg model
- Residual resistivity formulated in the Kubo-Greenwood linear-response theory with all quantities (matrix elements, Green-function elements) expressed in terms of Kohn-Sham orbitals and one-electron Hamiltonian
- Disorder-induced vertex corrections are included
- The Kubo-Greenwood theory neglects:
  1. the effect of phonons
  2. the effect of thermodynamical fluctuations related to the spin-spin correlation function G_{ij}

$$G_{ij} = < S_i.S_j > - < S_i > . < S_j >$$

- Effect of phonons $\Rightarrow$ weak monotonic increase of resistivity with temperature
- Effect of thermodynamical fluctuations $\Rightarrow$ resistivity varies with temperature and exhibits a maximum at the Curie temperature
- Present theory thus describes reliably the low-temperature limit of the resistivity where the impurity and/or magnetic-scatterings dominate

Bulk residual resistivity: TB-LMTO-CPA

- The conductivity tensor for spin λ ($\lambda = \uparrow, \downarrow$) ($\mu = x, y, z$):

$$\sigma_{\mu\nu}^{\lambda} \propto \mathrm{Tr}\,\langle g^{\sigma}(E_{\mathrm{F}}^{+})\rangle D_{\nu} \langle g^{\sigma}(E_{\mathrm{F}}^{-})\rangle D_{\mu} + \text{vertex part}$$

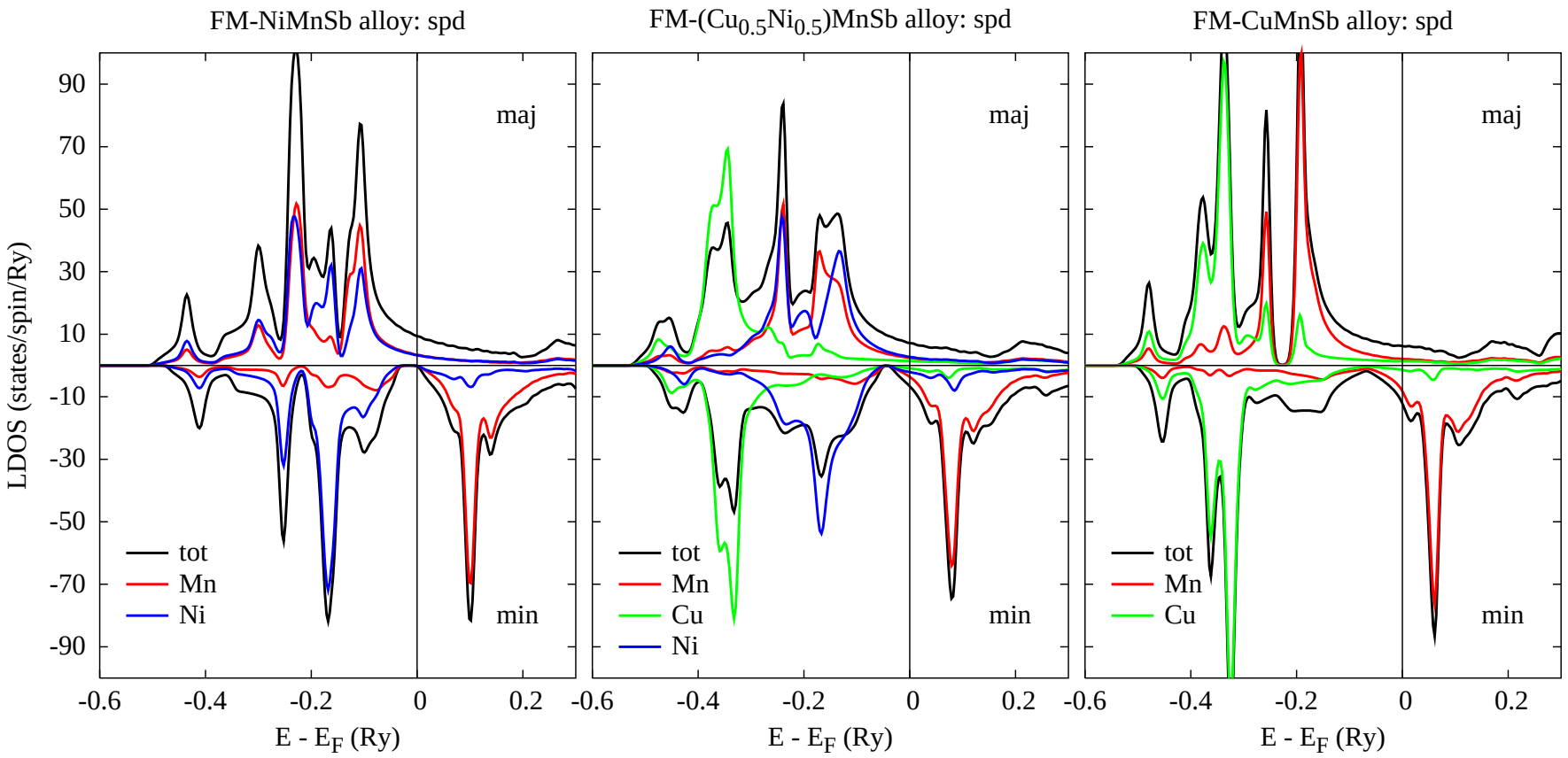
  where

$$D_{\mu} = [R_{\mu}, S]\ (\mu = x, y, x) \quad \text{is the effective velocity}$$

- present formulation leads to nonrandom velocity operator $\Rightarrow$ vertex part is obtained straightforwardly in the CPA method
- residual resistivity: $\rho_{\mu\mu} = 1/(\sigma_{\mu\mu}^{\uparrow} + \sigma_{\mu\mu}^{\downarrow})$
- Typical resistivity of concentrated metal alloys $\Rightarrow$

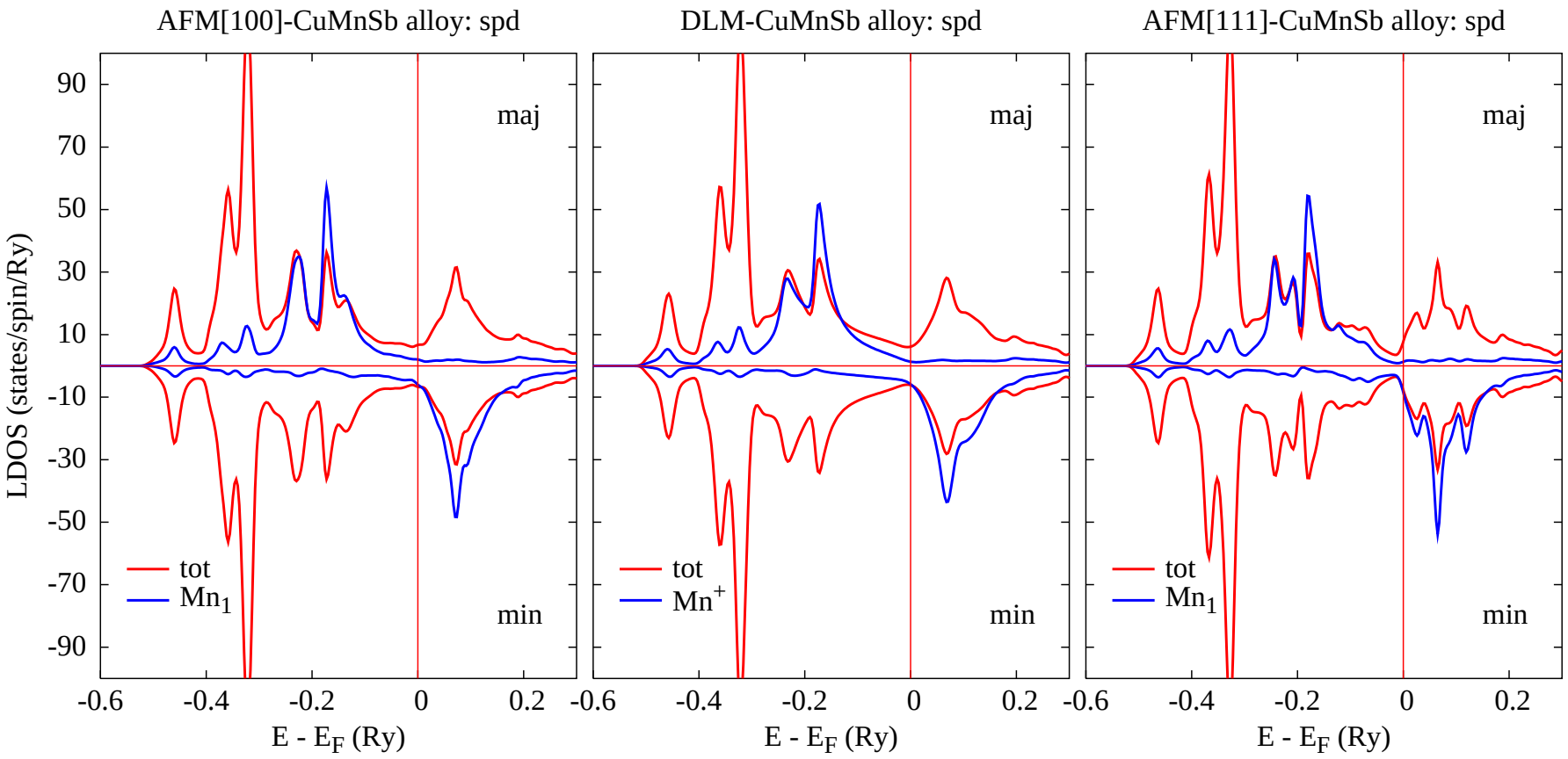
$$\rho \approx 0.1 \div 1 \times 10^{-6}\ \Omega\,\mathrm{m} \quad \text{or} \quad 10 \div 100\,\mu\Omega\,\mathrm{cm}$$

(Cu,Ni)MnSb alloys: electronic properties - LDOS



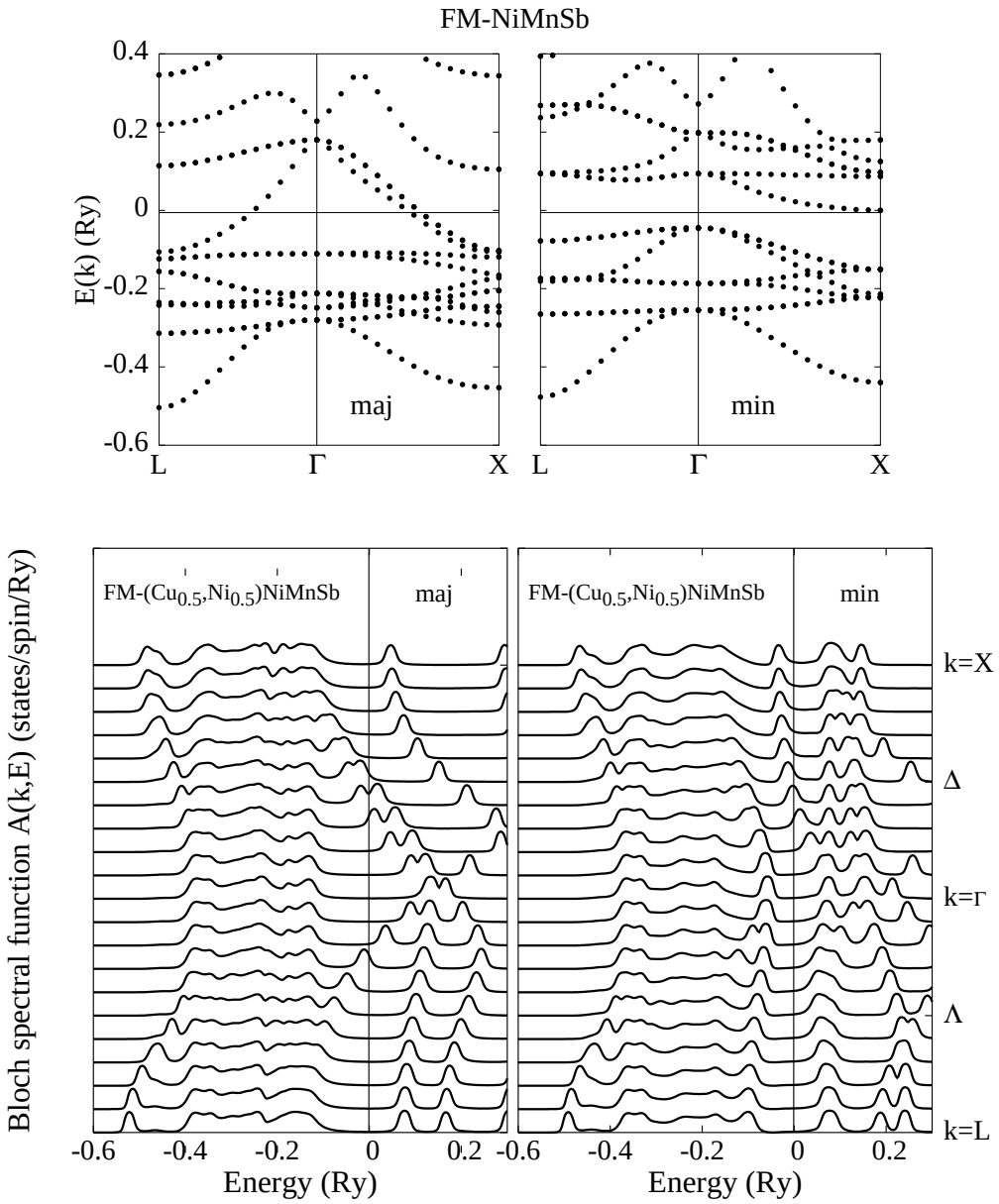
- Effect of alloying:
  1. halfmetallic behavior $\Rightarrow$ to metallic behavior
  2. E_f moves toward unoccupied Mn d-level
- Strong Cu-Ni disorder

(Cu,Ni)MnSb alloys: electronic properties - LDOS (cont.)

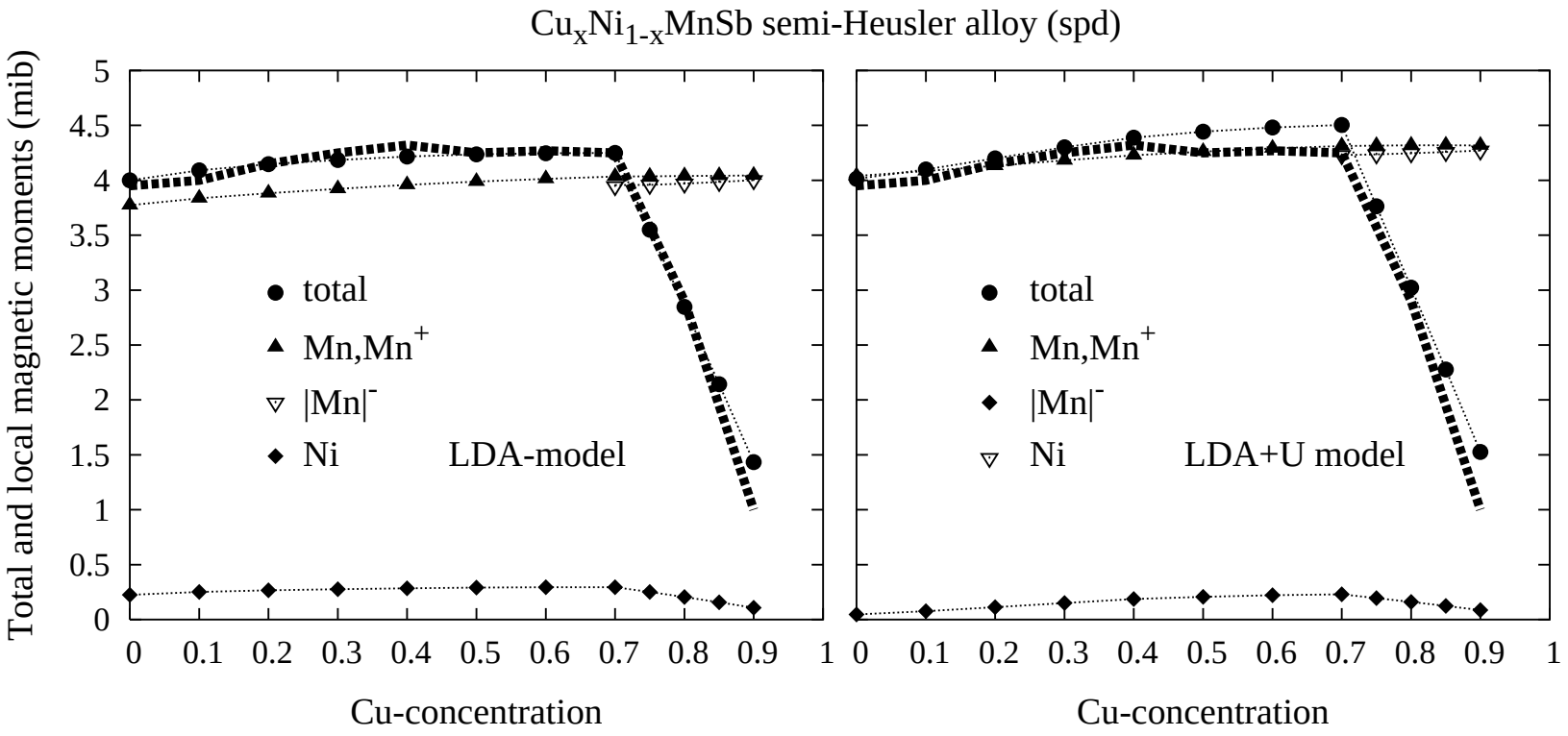


- Effect of magnetic arrangements: AFM with spin-orientations changing along [100]- and [111]-directions vs DLM-state for CuMnSb

(Cu,Ni)MnSb alloys: electronic properties - BSF

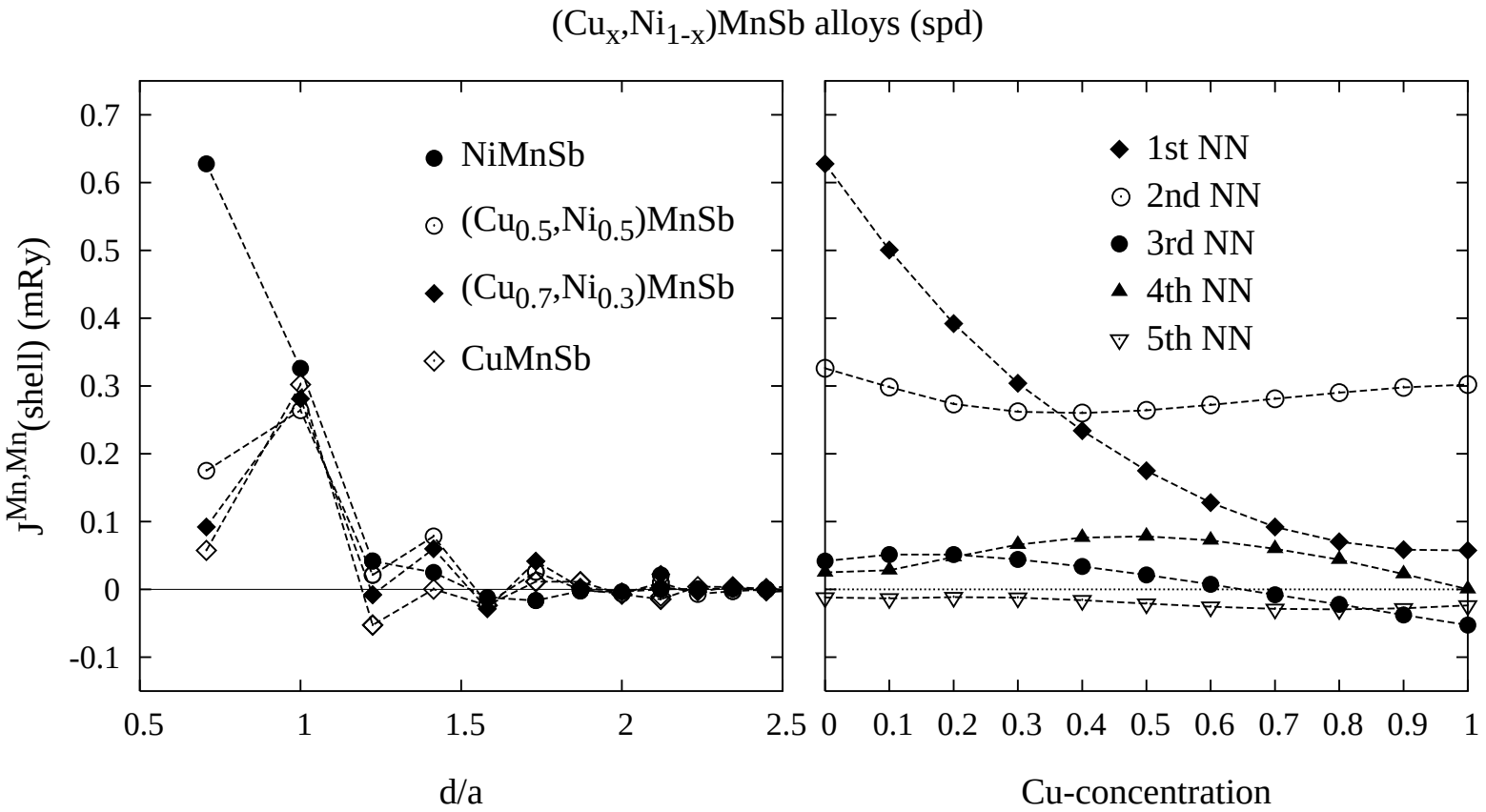


(Cu,Ni)MnSb alloys: magnetic properties



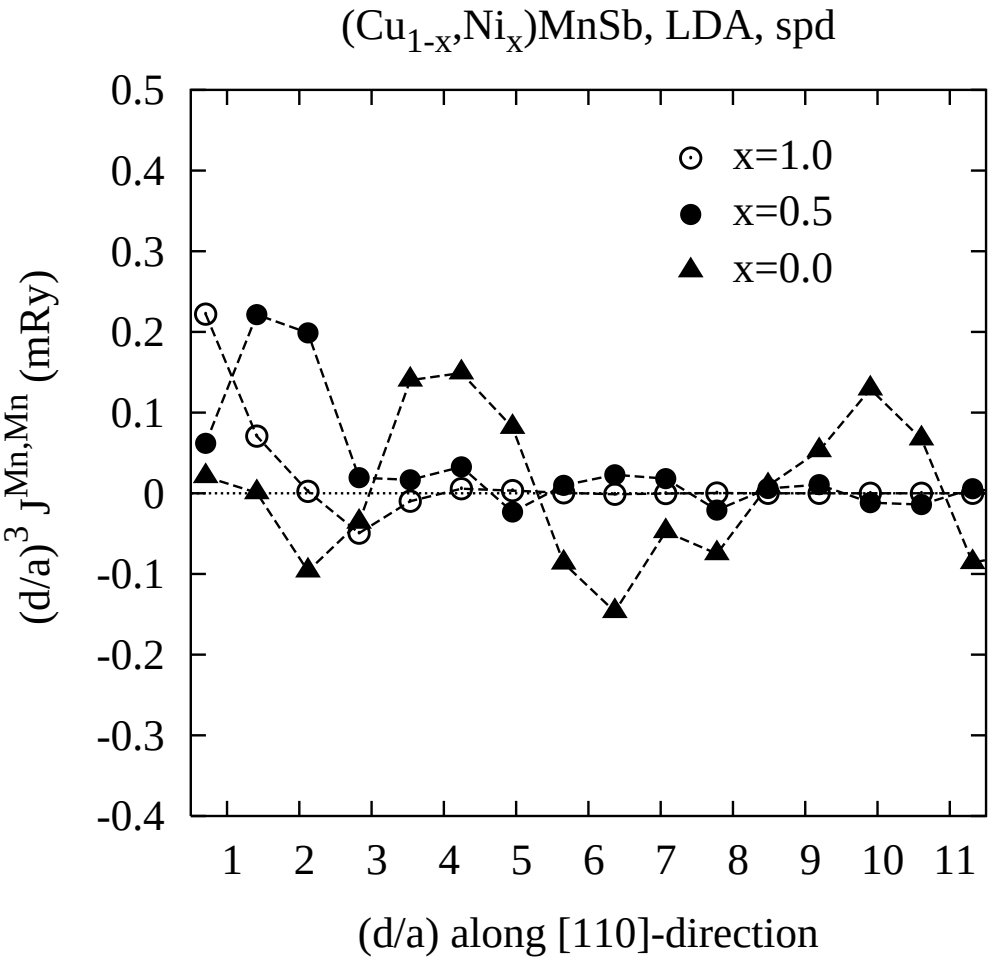
- Model: – ferromagnetic state for $x_{Cu} \leq 0.7$
  – uncompensated DLM state for $x_{Cu} > 0.7 \Rightarrow$
  $x^- = (5/3)\,(x - 0.7)$, i.e., the concentration of oppositely oriented spins increases linearly with x_{Cu}
  so that for $x_{Cu} = 1$ we have the DLM-state

(Cu,Ni)MnSb alloys: Mn-Mn exchange interactions



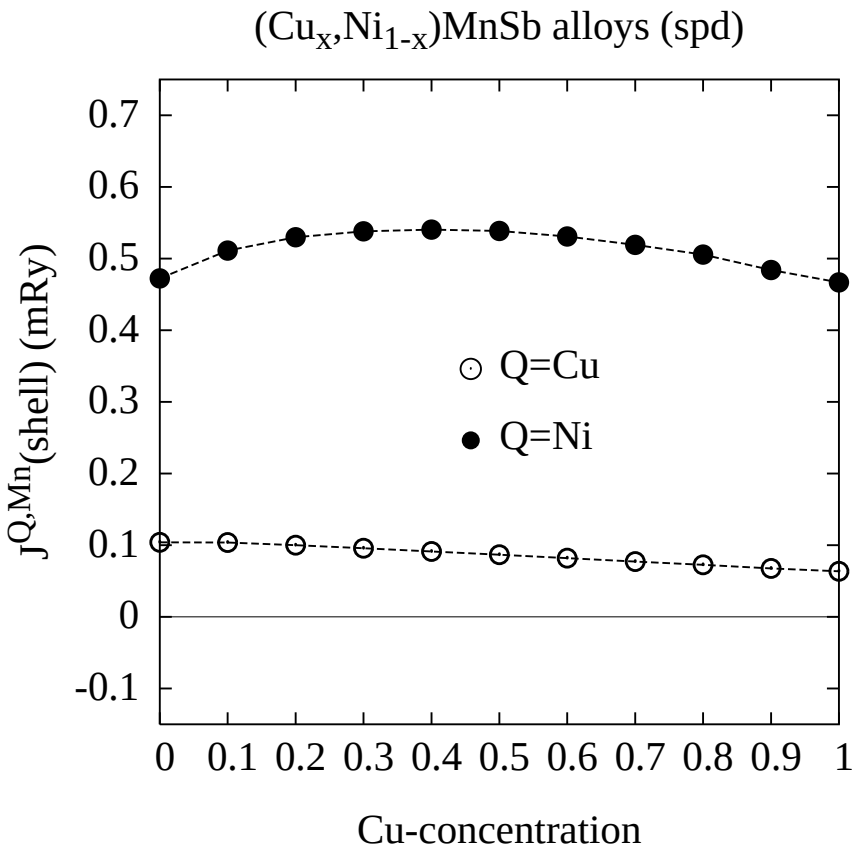
- Dominating exchange interactions depend weakly on composition with exception of 1st NN $\Rightarrow$ decreases due to increasing superexchange (E_f moves toward unoccupied Mn d-states)

(Cu,Ni)MnSb alloys: asymptotic behavior of $J_s^{Mn,Mn}([110])$



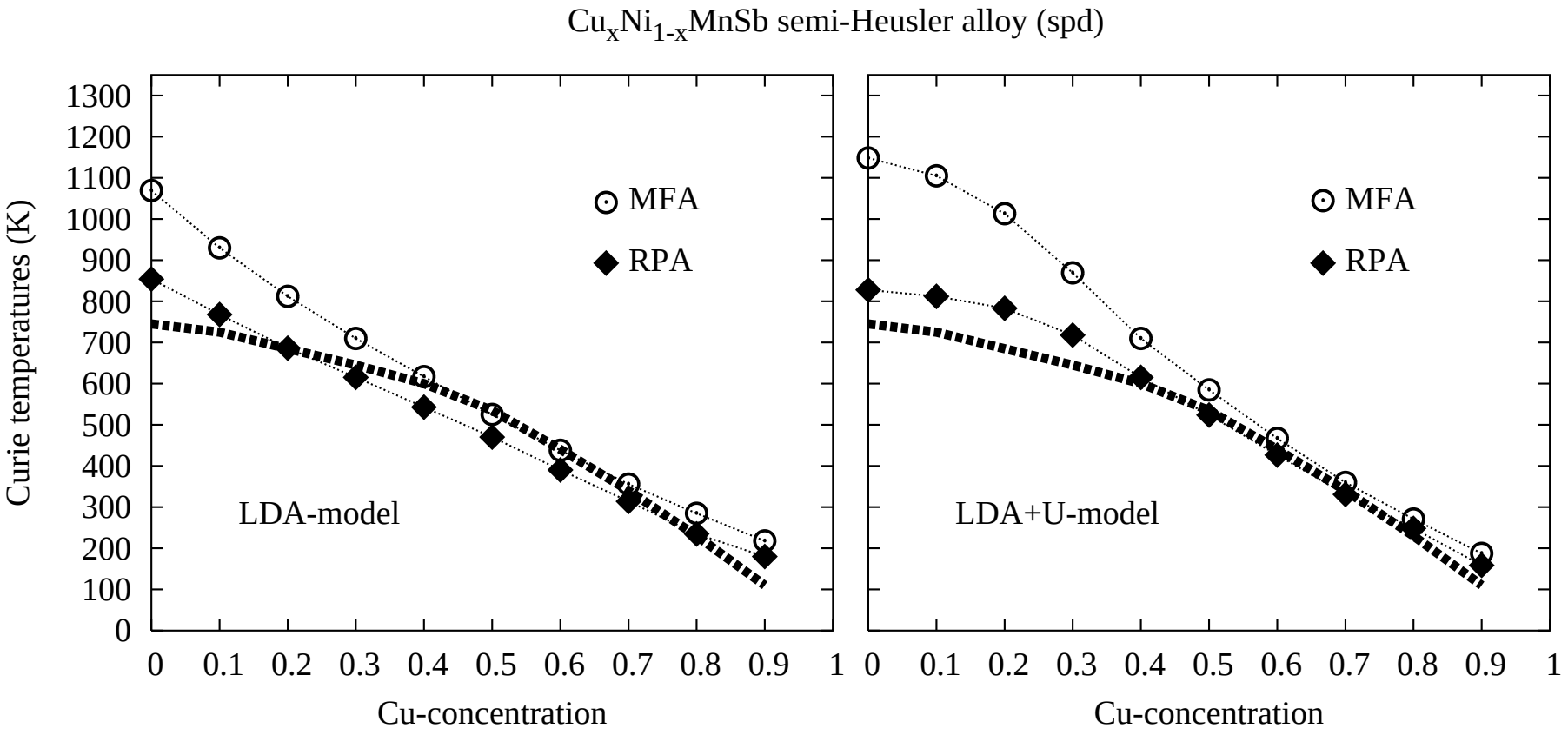
- Exchange interactions along [110]-directions dominate
- Halfmetal NiMnsb $\Rightarrow$ exponential damping
- Metal CuMnSb $\Rightarrow$ oscillatory behavior (RKKY-like)

(Cu,Ni)MnSb alloys: Q-Mn exchange interactions (Q=Ni,Cu)



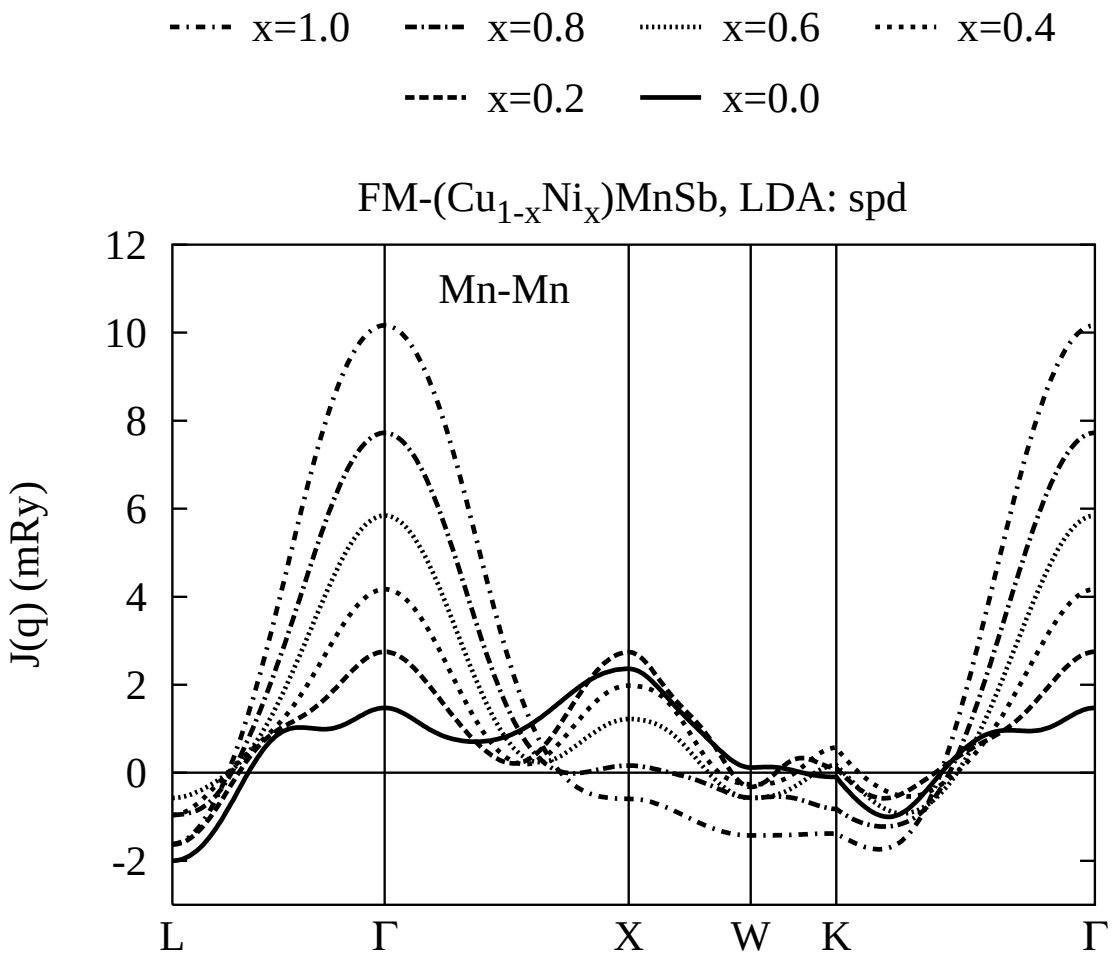
- Interactions are strongly localized (only 1st NN are relevant) and weakly concentration dependent
- Problem: interactions due to induced magnetic moments $\Rightarrow$ neglected (Sandratskii & Bruno 2007)

(Cu,Ni)MnSb alloys: Curie temperatures



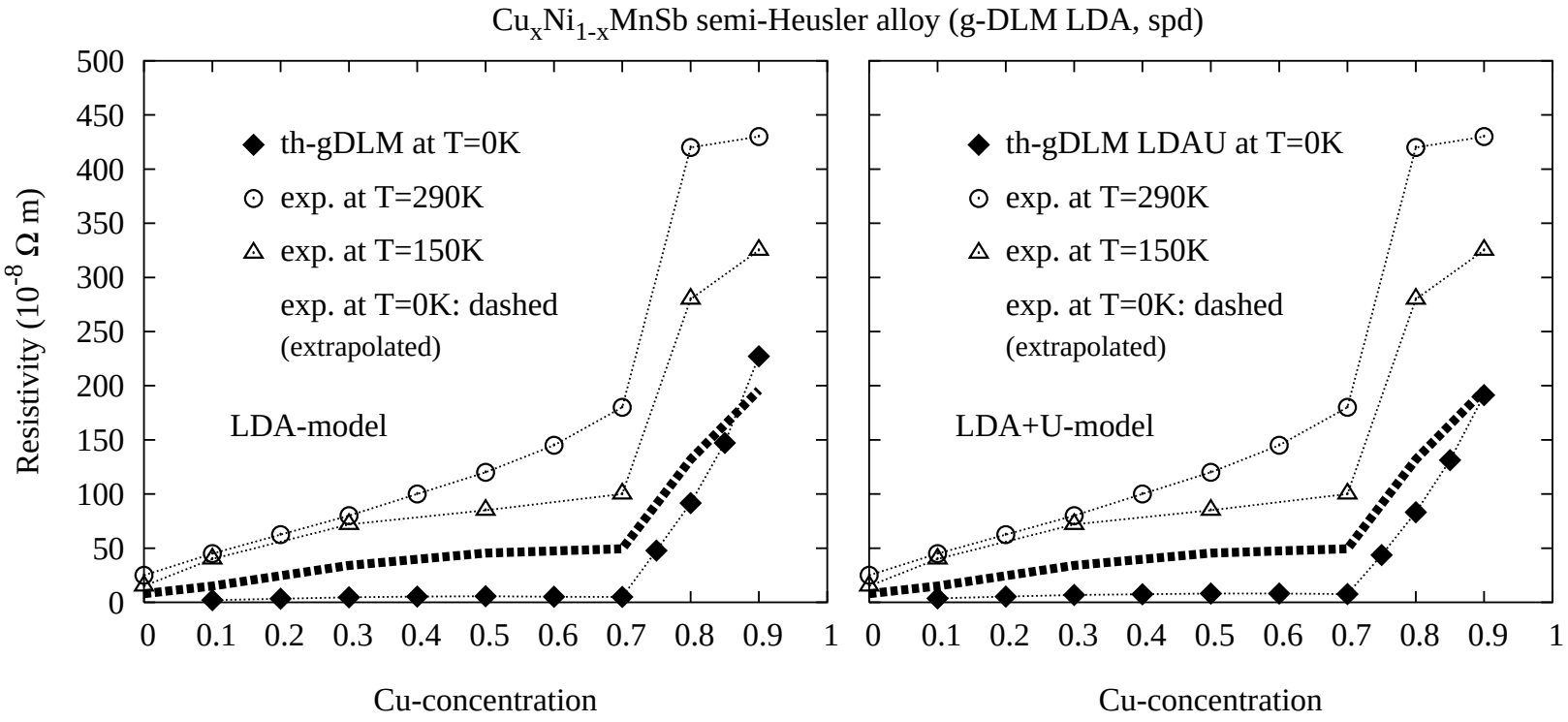
- RPA agrees reasonably with experiment (MFA overestimate T_c)
- LDA+U slightly improves agreement with experiment as compared to LDA

(Cu,Ni)MnSb alloys: magnetic stability



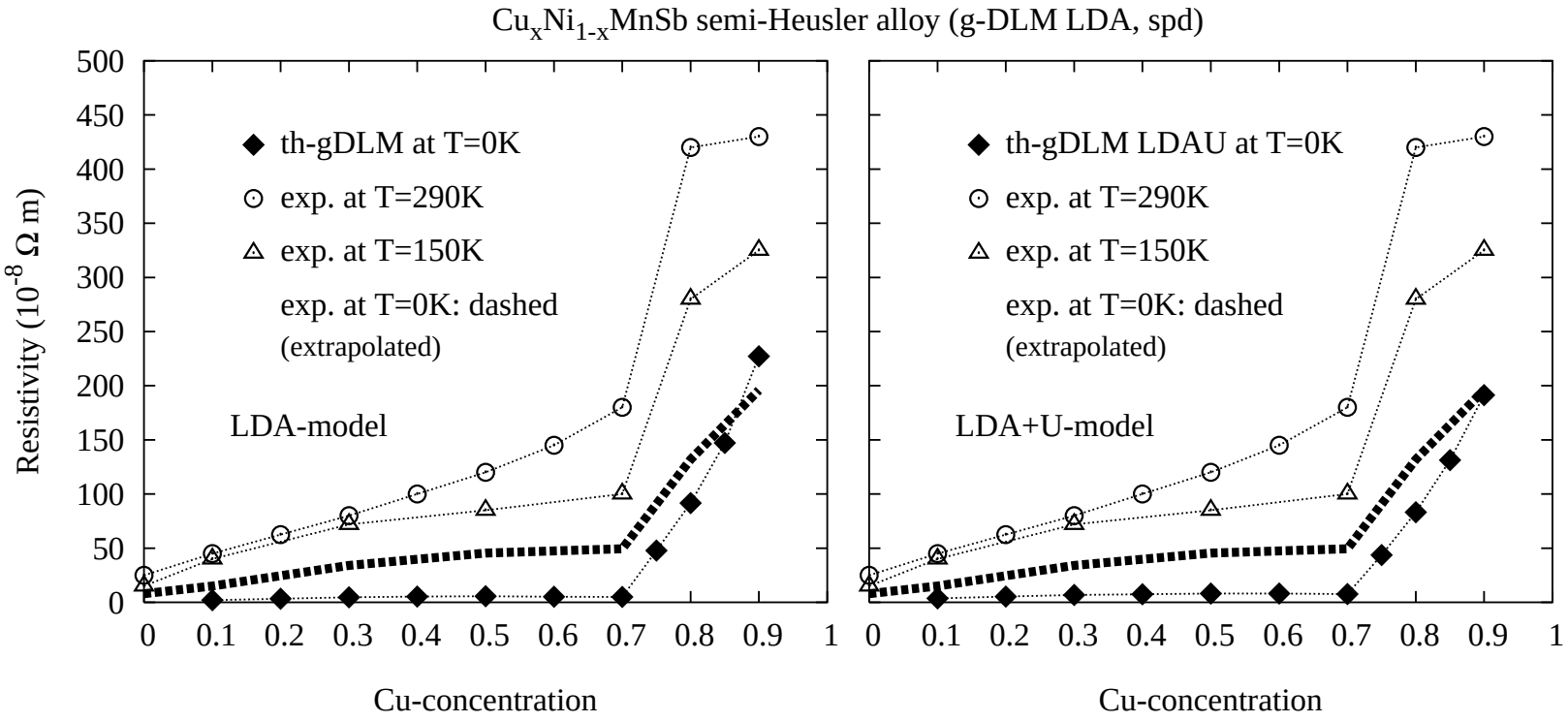
- Lattice Fourier transformation of exchange integrals ($J(\mathbf{q})$) indicates transition at about $x_{\mathrm{Cu}} \approx 0.7 - 0.8$

(Cu,Ni)MnSb alloys: residual resistivity (T=0K)



- Simple model (the same as for magnetic moments): ferromagnetism for $x_{Cu} \leq 0.7$ and uncompensated DLM for $x_{Cu} > 0.7$ explains concentration trend of residual resistivities
- Possible vacancies and interstitial/swapping defects can further increase exp. resistivity as compared to theoretical one

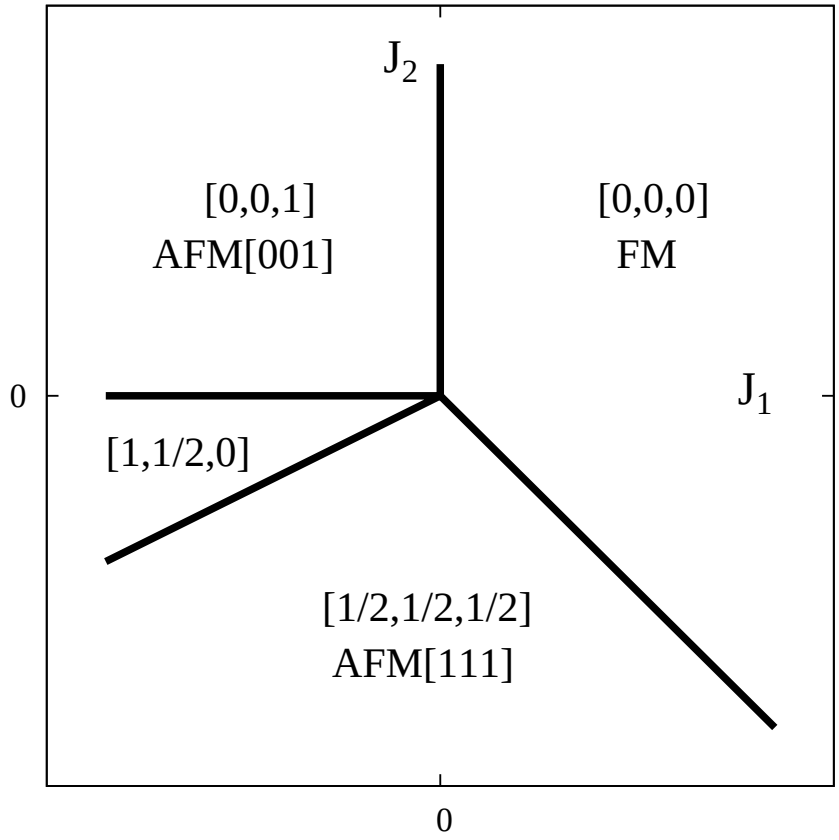
(Cu,Ni)MnSb alloys: residual resistivity (T=0K, AFM models)



- Alternative models of spin-disorder: AFM100/AFM111 with spin-disorder on one-sublatice for $x_{Cu} > 0.7$ also explains concentration trend of residual resistivities. $M_{tot}=f(x_{Cu})$ for both models is almost identical to uDLM model

CuMnSb alloy: magnetic ground state

- Experiment: AFM[111] $\Rightarrow$ simple fcc 2 NN-Ising model for AFM[111] requires $J_2 < 0$ while calculations give robust $J_2 > 0$, $J_1 \approx 0$ and thus lead to AFM[100]-ground state



CuMnSb alloy: magnetic ground state (cont.)

- Total energy calculations $\Rightarrow$ TB-LMTO (exp/th. lattconsts) and FP-LAPW (exp.lattconst) confirm AFM[100]-ground state

- Relativistic TB-LMTO (exp. lattconst) also confirm AFM[100]-ground state

- Variation of volume by 5% (increase/decrease) also leads to AFM[100]-ground state

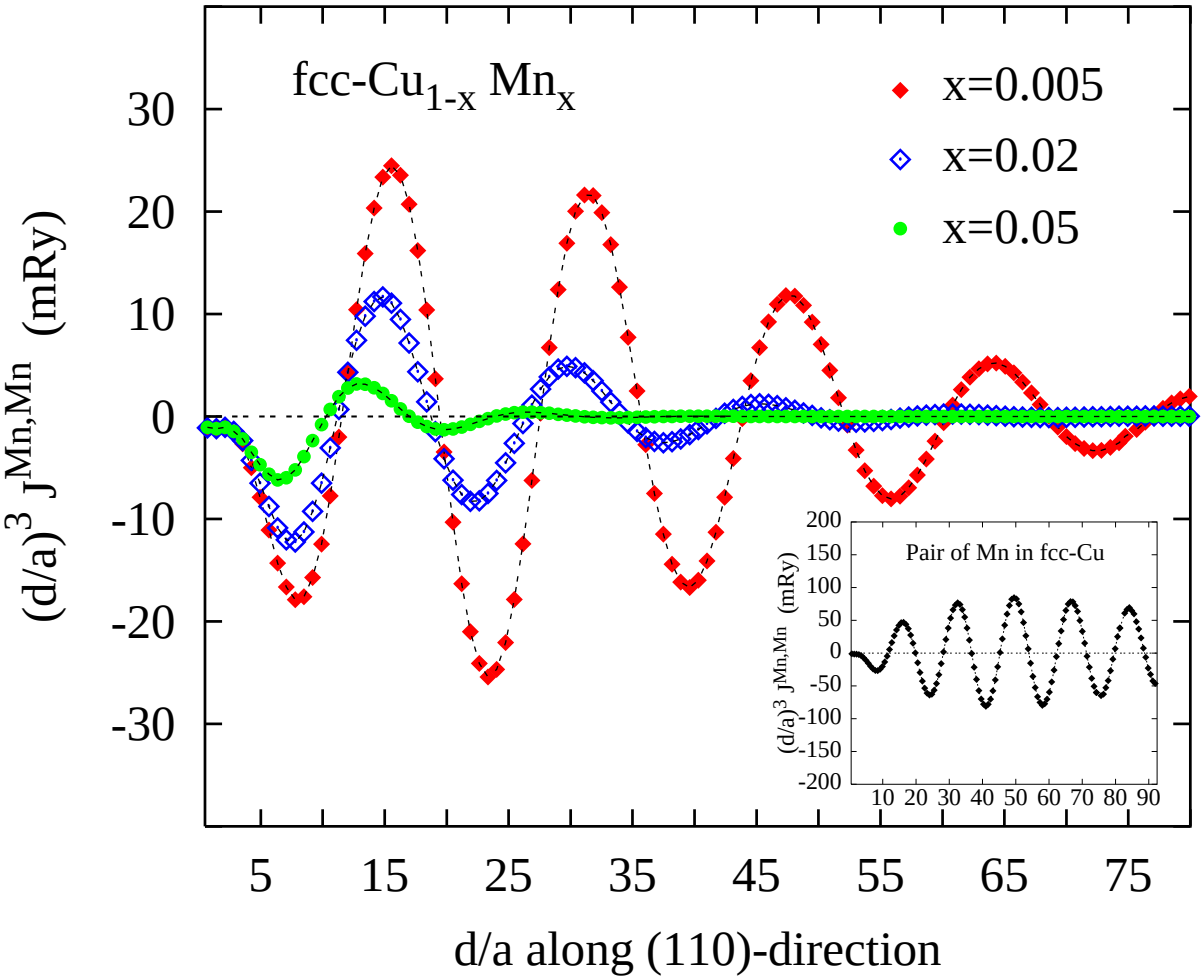
- TB-LMTO-LDAU lowers energy difference between AFM[100] and AFM[111] but AFM[100] is still-ground state

Origin of discrepancy is unknown (Jahn-Teller effect?)

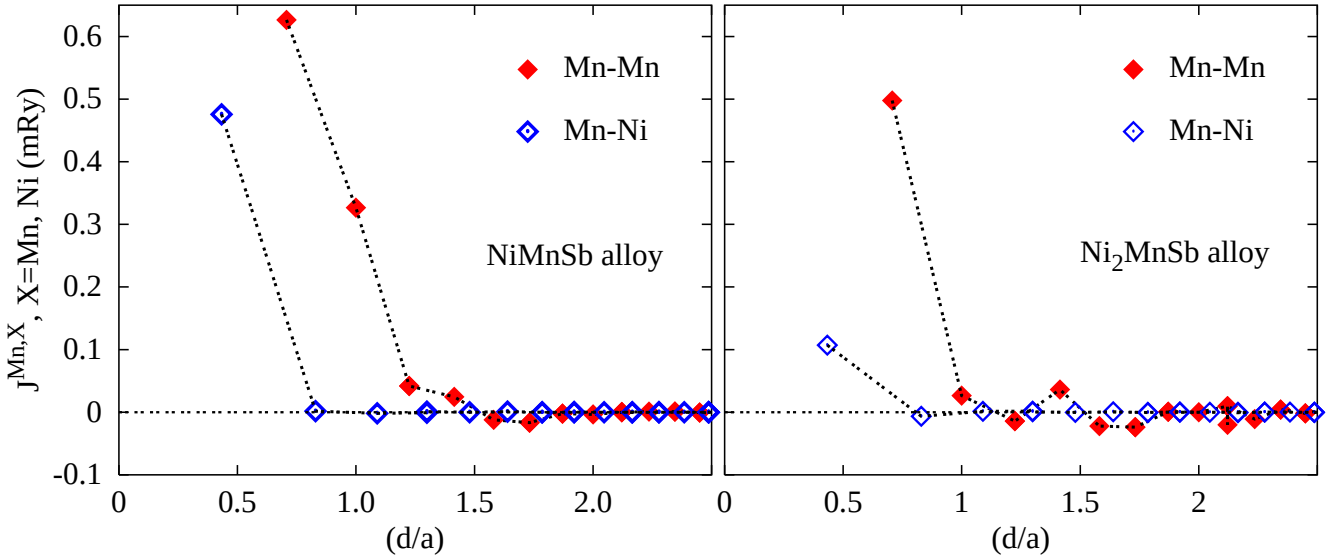
Conclusions: (Cu,Ni)MnSb semi-Heusler alloys

- First-principles study of a broad range of physical properties of quaternary semiHeusler alloys (Cu,Ni)MnSb including electronic, magnetic, thermodynamical, and transport ones has been presented
- The two-step procedure for determination of the alloy Curie temperature in the framework of the RPA was used
- Residual resistivity of alloys has been determined using Kubo-Greenwood linear-response approach
- The abrupt change in concentration dependences of magnetic moments and resistivities can be explained by a gradual FM to AFM transition due to magnetic disorder on Mn-sublattice modelled as uncompensated DLM state
- Overall good quantitative agreement between theory based on a unified model without adjustable parameters and experiment has been obtained
- Open problem: magnetic ground-state of CuMnSb

Exchange integrals: effect of disorder



Exchange intergrals: effect of halfmetallicity



CURIE TEMPERATURES:

	NiMnSb	Ni_2MnSb
MFA:	1106 K	575 K
RPA:	880 K	360 K
MCS:	910 K	380 K
RPA(*)	852 K	356 K
Exp:	732 K	363 K

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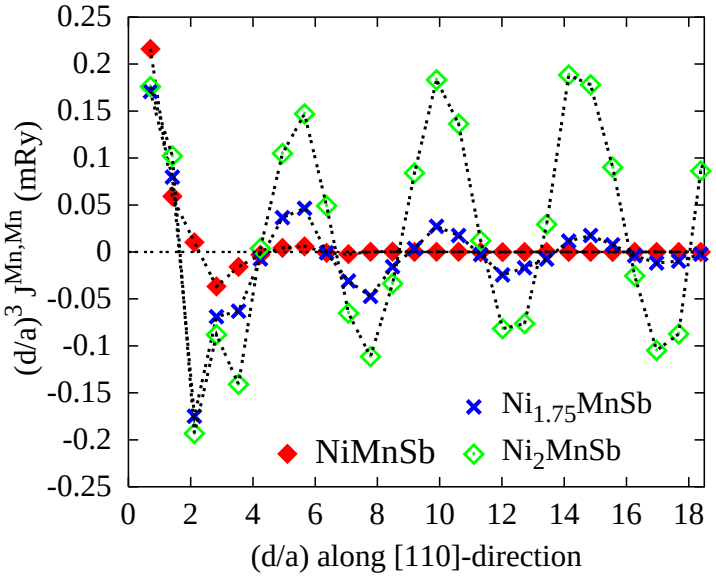
MCS and RPA(*)are obtained by neglecting Mn-Ni interactions



Example of residual resistivity: AgPd alloy