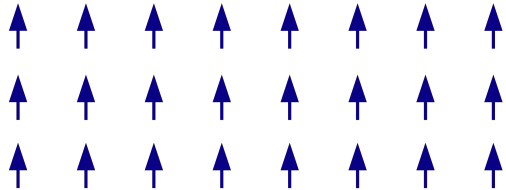# Magnetism of 3d metals and alloys with GreenALM

Magnetism of d-metals
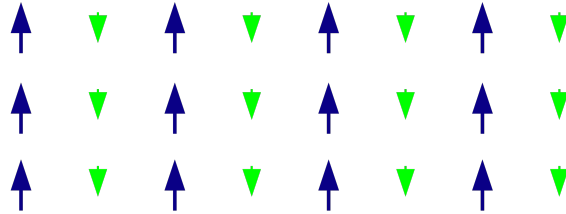
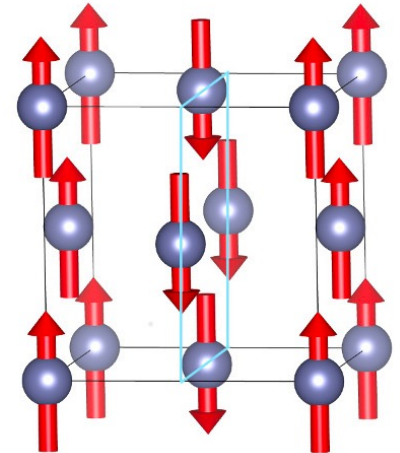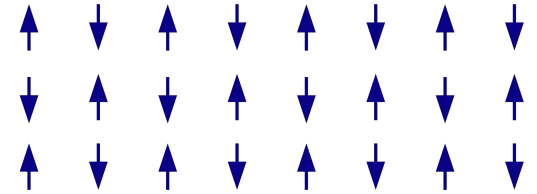|									
3d	Sc hcp	Ti hcp	V bcc	Cr AF, SDW bcc	Mn AF Mn	Fe FM bcc	Co FM hcp	Ni FM fcc	Cu fcc
4d	Y hcp	Zr hcp	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh fcc	Pd fcc	Ag fcc
5d	La (Lu)	Hf hcp	Ta bcc	W bcc	Re hcp	Os hcp	Ir fcc	Pt fcc	Au fcc

Magnetic structures
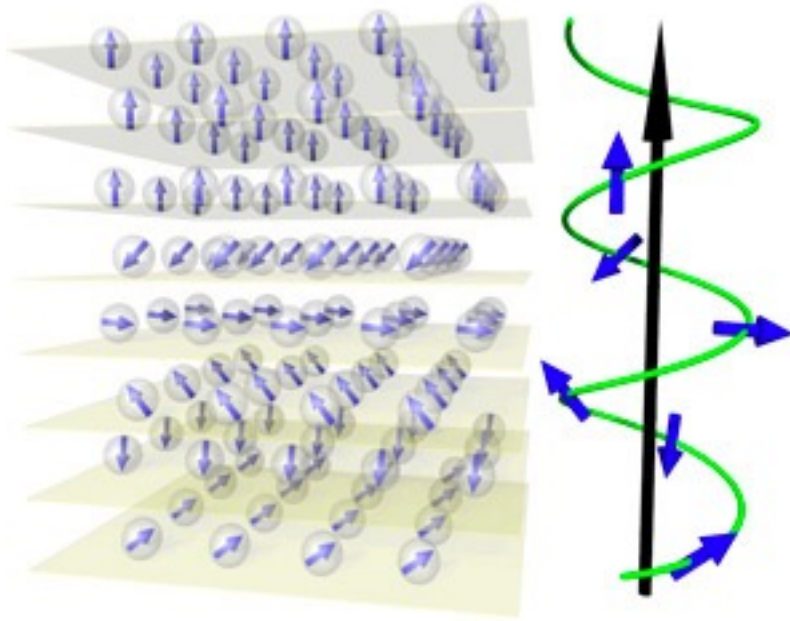
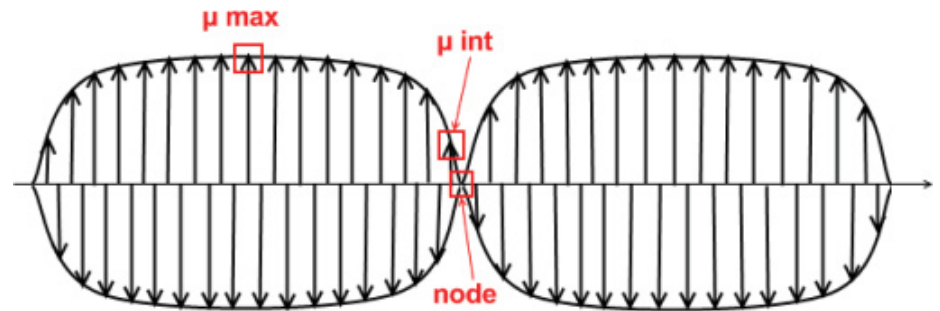## Ferromagnetic state

Ferrimagnetic state

Antiferromagnetic state

Magnetic structures

Spin-spiral structure

Cr ground state magnetic structure: antiferromagnetic spin density wave

μ max

μ int

node

Magnetic density in 3d metals

Magnetization density (collinear): $m(\mathbf{r}) = \rho^{\uparrow}(\mathbf{r}) - \rho^{\downarrow}(\mathbf{r})$

Internal Magnetization Density Distribution of Iron and Nickel by the Maximum Entropy Method

Ludwik Dobrzynski,[1,2] Robert J. Papoular[3,4] and Makoto Sakata[5]
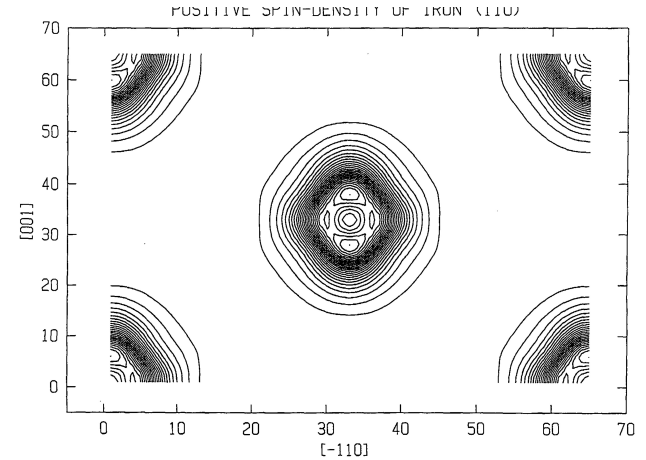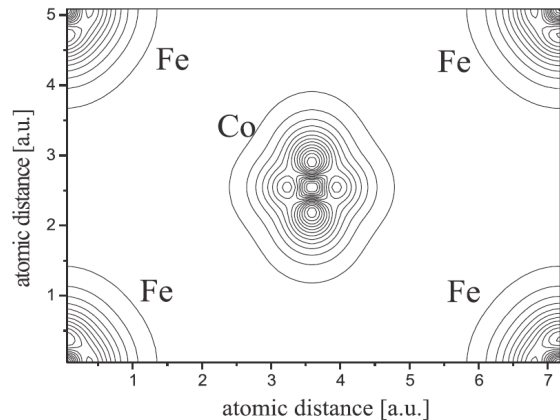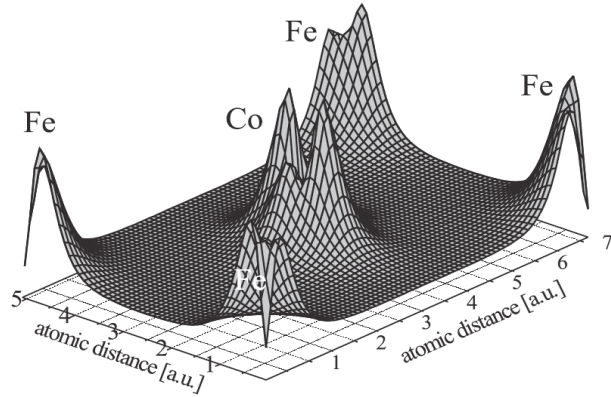
POSITIVE SPIN-DENSITY OF IRON (110)

Fig. 11. Positive part of magnetization-density distribution of iron in the (110) plane, calculated with P-MEM code. Contours are ploted from 0.1 in steps of 0.1.

Magnetic density is quite strongly localized on atoms

Local atomic magnetic moment

$$\mathbf{m}(\mathbf{r}) = \sum_{\alpha\beta} \vec{\sigma}^{\alpha\beta} n^{\alpha\beta}(\mathbf{r})$$

magnetic density

Local atomic magnetic moment

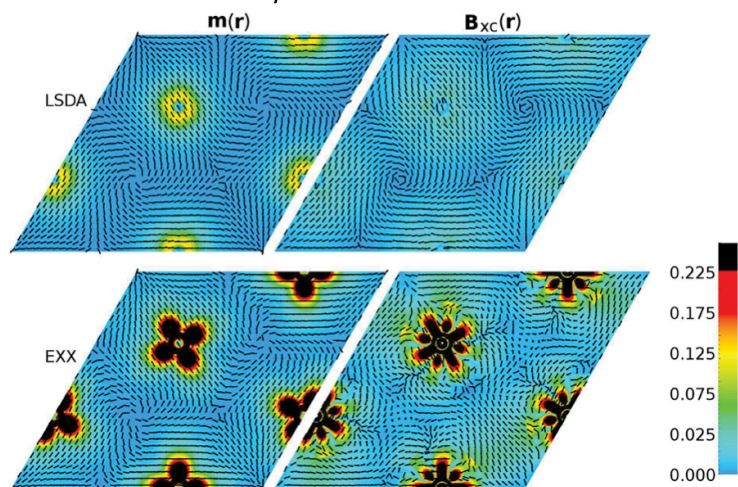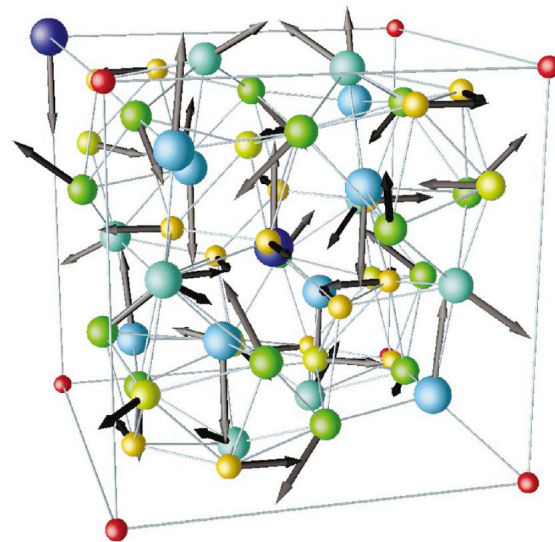$$\mathbf{m}(\mathbf{R}) = \int_{S_\mathbf{R}} \mathbf{m}(\mathbf{r})d\mathbf{r}$$


FIG. 1 (color). Fully noncollinear magnetization density and **B** field obtained using the LSDA and exchange-only EXX functionals for an unsupported Cr monolayer in Néel state. Arrows indicate the direction, and information about the magnitude (in atomic units) is given in the color bar.

S. Sharma, PRL 2007

Crystalline and magnetic structure of Mn (D.Hobbs, et al. PRB 2003)

T = 0 K: DFT (LSDA or GGA) works fine for 3d metals
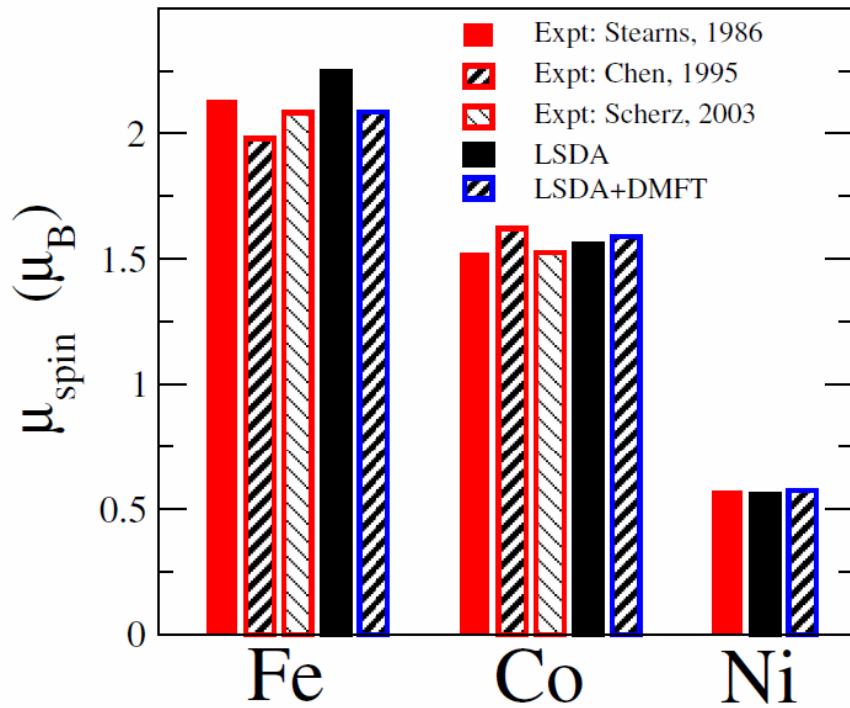
If the lattice constant experimental one... and if GGA-PW functional is used.

GGA-PBE slightly overestimates magnetic moments and probably magnetic energy, which is ~m² (in the case of Fe the difference is about 30 meV (360 K).

Magnetism in DFT at finite T

Although the origin of magnetism is a spin of an electron, i.e. magnetism almost totally related to electronic structure, it is practically not included in finite T DFT (Mermin, 1965).

This means that it should be modelled separately.
This can be done in two ways:
1) Using classical Heisenberg Hamiltonian, which can be used in statistical simulations:
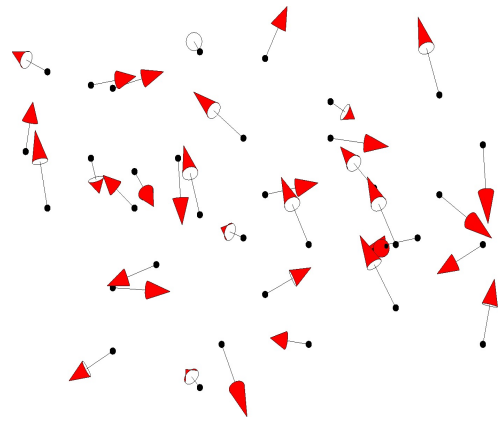
$$H_{mag} = -\sum_{ij} J_{ij} \vec{\sigma}_i \vec{\sigma}_j + \dots \quad i \text{ and } j \text{ are sites;} \quad \vec{\sigma}_i \text{ is the unit vector in the direction of } \mathbf{m}(\mathbf{R}_i)$$

2) Some specific configuration of atomic magnetic moments modelling the given magnetic state can be used in DFT calculations.
3) Do something else…. or… just DMFT calculations…

Paramagnetic state: disordered local moments (DLM)

Spin-spin correlation function for the p-th coordination shell:

$$\xi_p = \frac{1}{N} \sum_{\mathbf{R}_j \subset p} \mathbf{e}_i \mathbf{e}_j$$

Ideal paramagnetic state corresponds to $T \to \infty$

for which $\quad \xi_p^{IP} = 0 \;\; \text{for all } p$

That is, the directions of the spins at different sites are pointing randomly to different directions.

However, in the absence of the spin-orbit interaction, this state can be modeled exactly by disordered local spin-up and spin-down magnetic moments (DLM) at different sites:

$$A_{0.5}^{\uparrow} A_{0.5}^{\downarrow}$$

DLM model represents a random alloy of "spin-up" and "spin-down" atoms, whose electronic structure and energy can be obtained by methods for random alloys.

Advantage of DLM modeling with CPA

homogeneous representation of the PM state,
which is very important especially for Fe and its alloys due to very strongly
coupling between local structure (atomic configuration) and local spin state.

such a representation is especially advantageous for multicomponent and
structurally inhomogeneous systems.

**the electronic structure is OK: electronic state are NOT Bloch states: they
are exponentially decaying in space (have finite life time)**

Itinerant vs localized magnetism

Unfortunately, DLM is a good model of paramagnetic state only in the case of localized magnetism, i.e. when magnitudes of magnetic moments do not fluctuate and little dependent on the magnetic state (which is, for instance, the case of Cu-rich CuMn alloys).

Most 3d-metals and alloys do not belong here: they are usually itinerant (or even weak itinerant) magnets. At finite temperatures, not only the direction of magnetic moments fluctuates (transverse fluctuations) in these systems, but the magnitude of magnetic moments also fluctuates too ("longitudinal spin fluctuations").
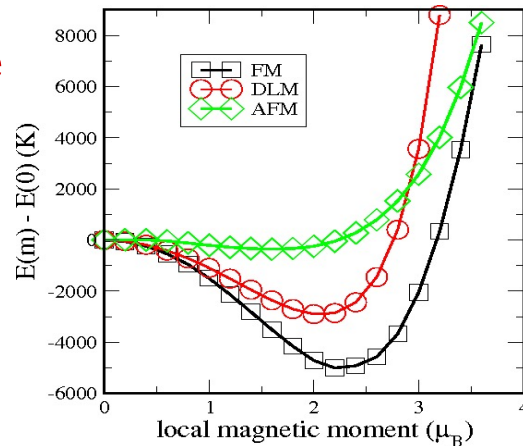
The reason for that is clear if one checks how the energy of the DLM state depends on the magnitude of magnetic moment.

The energy of magnetic state in bcc Fe and fcc Ni

From Moriya (1985)

Longitudinal spin fluctuation energy

From DFT:

Fe

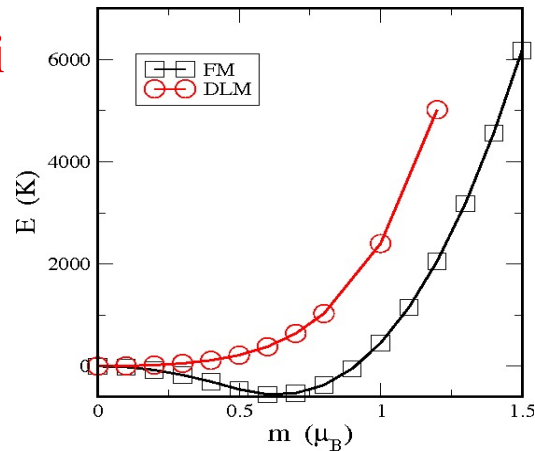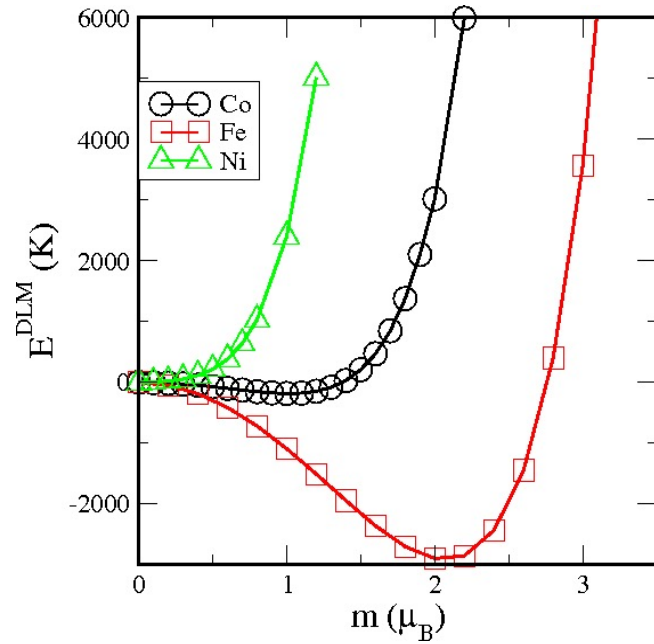**Ni**
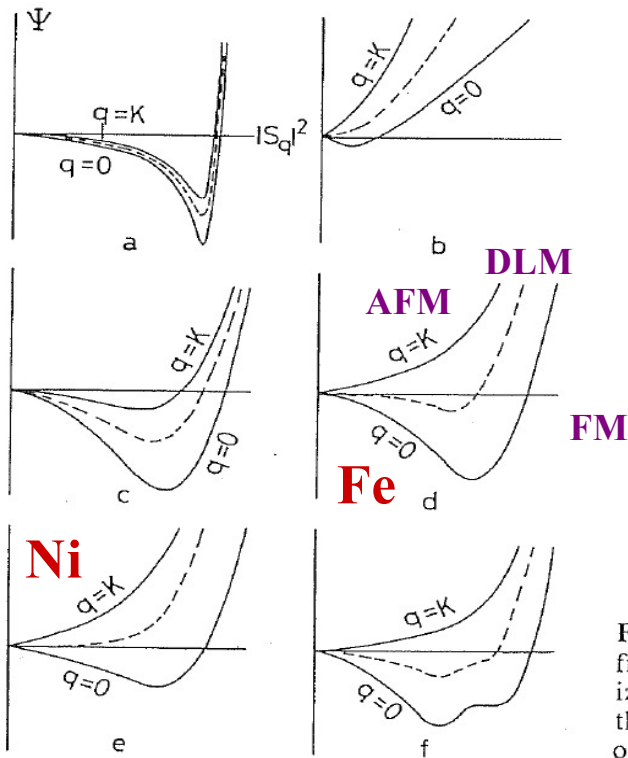
DLM
AFM
FM
Fe
Ni

Fig. 7.4. Some typical examples of the free energy variation due to spin polarization. The dashed lines correspond to the spin configurations with randomly oriented local moments

Longitudinal and transverse degrees of freedom

Local magnetic moment in DFT: $\quad m_i = \left(m_{xi}^2 + m_{yi}^2 + m_{zi}^2 \right)^{1/2}$

LSF energy in Co, Ni and Fe

This simple connection, however, does not give a clue how these degree of freedom are energetically distributed and coupled at high temperature (which is, for instance, can be obtained in DMFT calculations).

One can only argue, that in the case of "localized" magnetism (like bcc Fe), the transverse fluctuations are much more energetically favorable than longitudinal, which imposes a certain restrictions on m_x m_y and m_z.

Vice versa, for weak itinerant magnets (Ni, Co), the transverse fluctuations are the result of the fluctuations of the m_x m_y and m_z components: full coupling mode.

Simple model of LSF (for using in DFT)

In the case of Fe (localized limit)

$$Z^L = \int \exp\left[-E(m)/T\right] dm$$

In the case of Ni, Co (itinerant limit)

$$Z^I = \int m^2 \exp\left[-E(m)/T\right] dm$$

$$E(m) = am^2 + bm^4 + \ldots$$
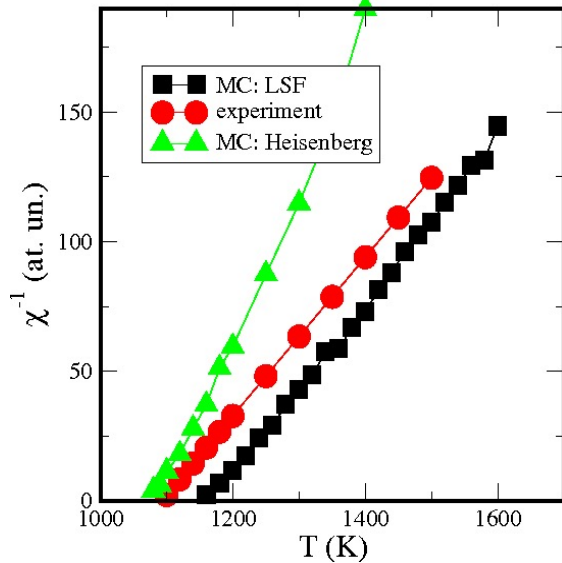
Leaving only quadratic term, one gets:

$$S^L = \ln(\langle m \rangle)$$

$$S^I = 3\ln(\langle m \rangle)$$

$$\langle m \rangle = \frac{1}{Z} \int m^{\square+1} \exp\left[-E(m)/T\right] dm \;\; ; \;\; \square = 2 \text{ (I) or } 0 \text{ (L)}$$
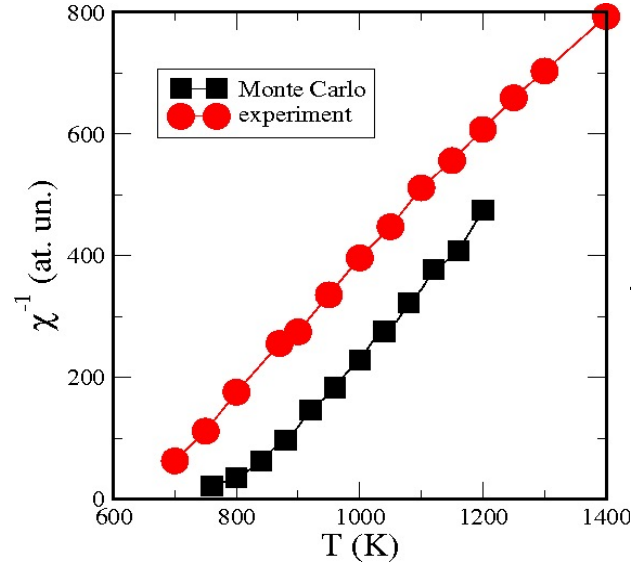
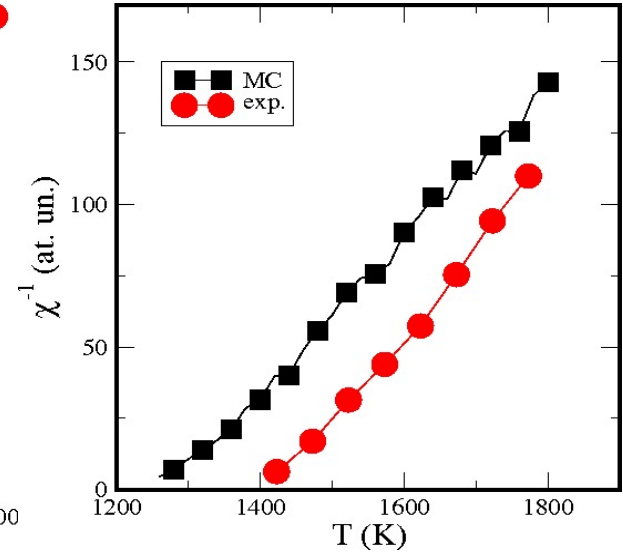# Paramagnetic susceptibility of Fe, Ni, and Co from LSF-MC simulations (unpublished)
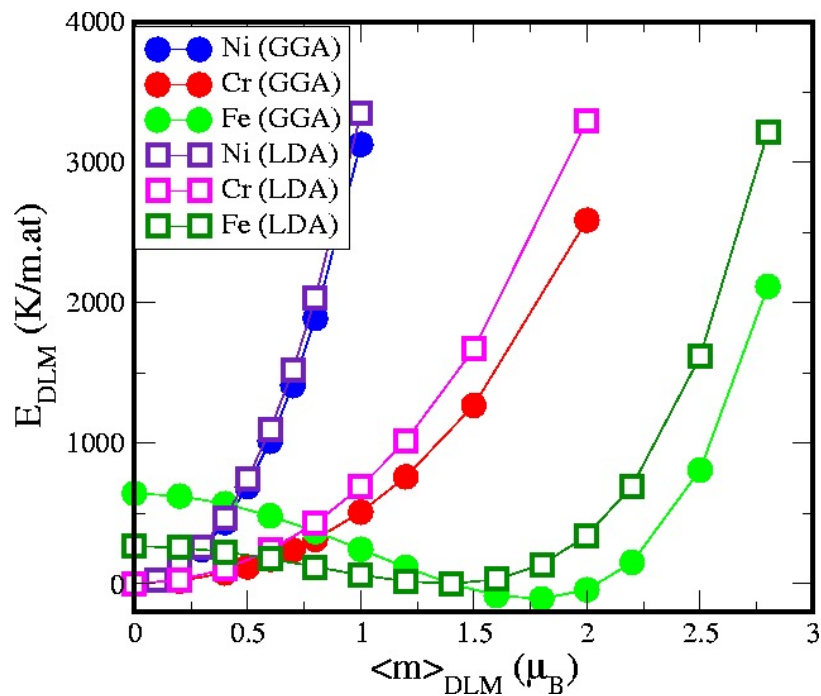

bcc Fe

fcc Ni

fcc Co

"localized" limit
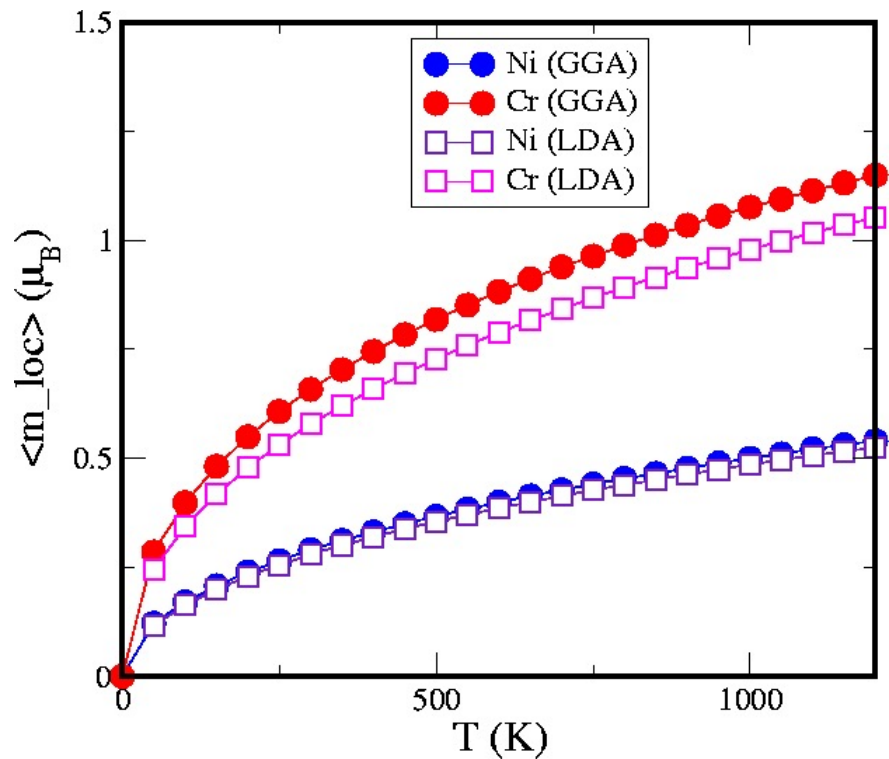
Weak itinerant limit

LSF induced magnetic moment in austinite: fcc Fe-20Cr-20Ni alloy
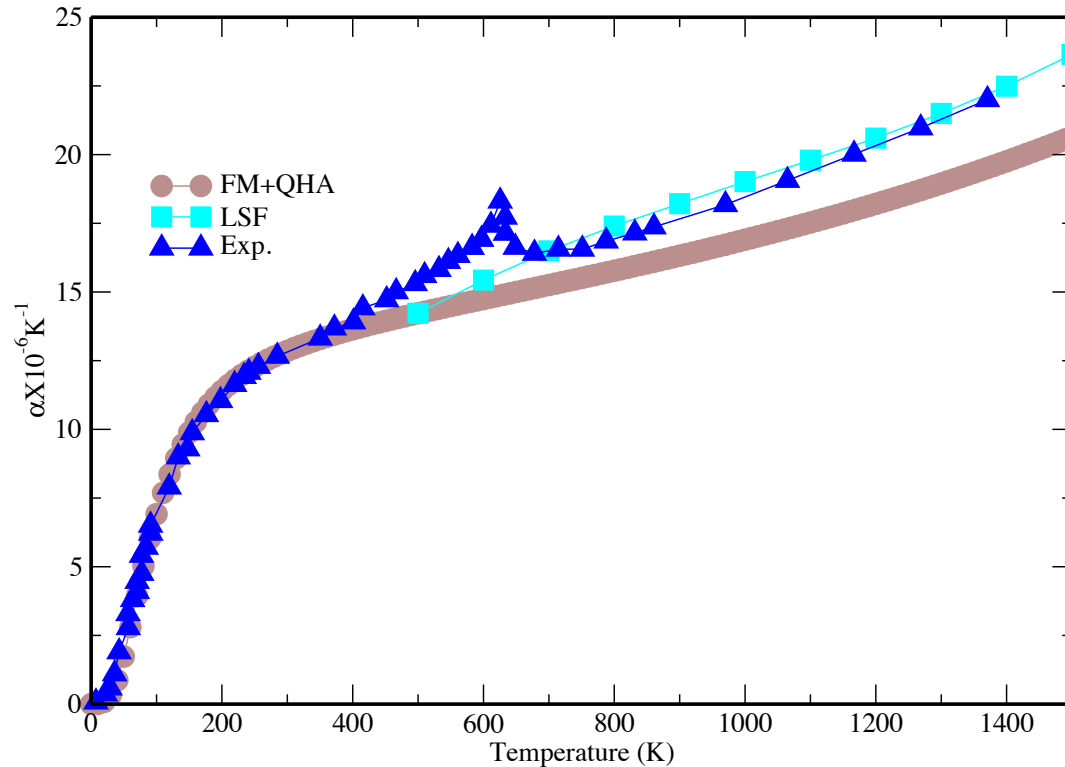
LSF energy (CPA calculations)

Magnetic moment of Ni and Cr

Thermal lattice expansion in Ni: effect of longitudinal spin fluctuations

Longitudinal spin fluctuations (LSF)

LSF can strongly affect some properties of 3d-metal alloys. They are responsible for

1) relatively large lattice constant of austenitic steels (cannot be reproduced in DFT calculations without their account);

2) anti-Invar effect in some Fe-Mn alloys (unusually large thermal expansion in certain range of temperatures);

3) they provide substantial contribution to enthalpies and free energies in some alloys; properties;

4) they can strongly affect elastic and mechanical properties of alloys.

LSF in DFT

It should be done in the DLM-CPA calculations (one-shot calculations in Hamiltonian formalism probably can be done using SWM, but it has never been properly tested).

The average magnetic moment can be obtained in a single self-consistent calculations using Pavel Korzhvyi's trick (Phys. Rev. B96, 224406 (2017)):

$$V_{\uparrow(\downarrow)}^{\text{LSF}} = \frac{\delta(-TS)}{\delta m} = +(-)\frac{T}{\alpha m} \quad ; \quad \alpha = \ 1\ (\text{L}) \text{ or } 3\ (\text{I})$$

DLM and LSF-DLM calculations in GreenALM

[Alloy]

mom	*<float>*	0.0	Initial spin splitting or magnetic moment (*lsm_mode = fxm*)
lsm_mode	*<string>*	**none**	Local spin moment mode: **none**, **fxm**, **dlm**, **lsf**
lsm_params	*<integer>*	3	LSF effective dimension: 1, 2, or 3

lsm_mode = dlm, lsf