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First principles electronic structure calculation and simulation of radiation defects evolution in plutonium by the density functional theory and the molecular dynamics approach

Computer simulation of

the electronic structure and magnetic

properties of actinides

by modern calculation methods

without any adjustable or empirical parameters such as ***ab initio***:

LDA, LDA+U, LDA+U+SO, LDA+DMFT

Computer simulation of

the phase stability at finite temperatures and

the effect of low-concentration impurities on thermodynamic and mechanical

properties of actinides

by Classical Molecular Dynamics (CMD),

including the case when inter-atomic potentials used in it are constructed

basing on the results of *ab initio* electronic structure calculations

Why there are so many ab initio *methods?*

LDA: electron-electron correlations are treated as for the uniform non-interacting electron gas. When electron-electron interaction becomes so strong that electronic states lose any resemblance to non-interacting electron gas, then one can speak about “strong electron-electron correlations”.

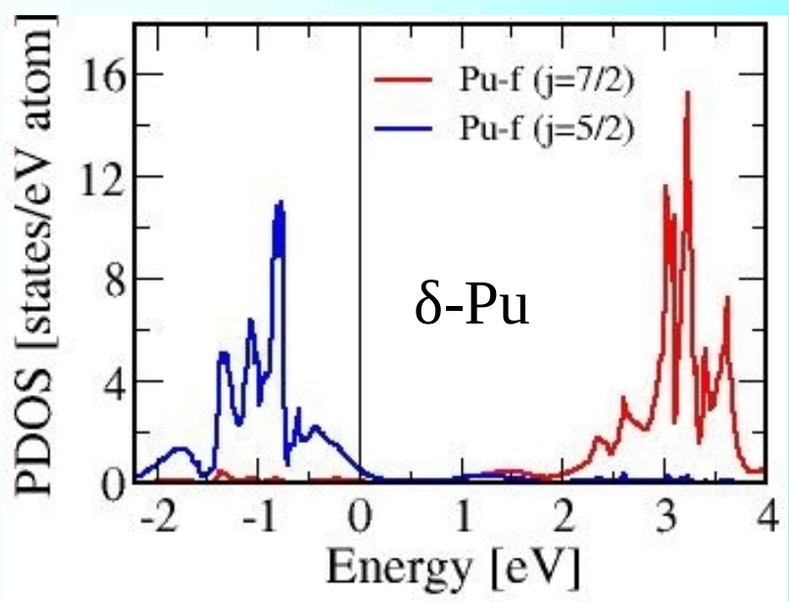
LDA+U: the correlations beyond the LDA are taken into account using the ideas of Hubbard model. In dependence on ratio U/W value between on-site Coulomb interaction **U** and the energy bands width W one can observe various regimes of electrons correlations from weakly correlated for $U/W << 1$ to strongly correlated for $U/W >> 1$. The results correspond to the ground state of the system for T=0: *electron-electron correlations are static*.

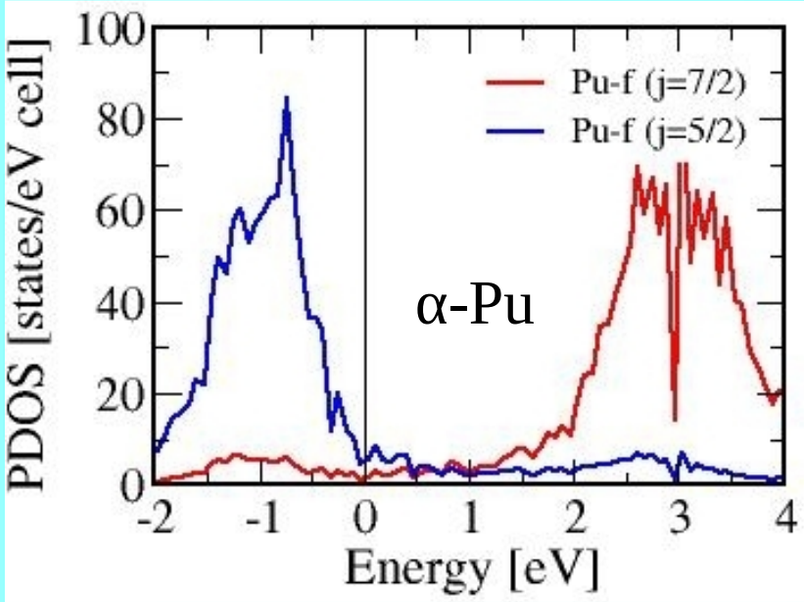
LDA+U+SO: takes into account a strong spin-orbit (**SO**) coupling in addition to magnetism and Coulomb interactions since the strengths of spin-orbit coupling and exchange interaction are comparable in 5*f* shell.

LDA+DMFT: the correlations beyond the LDA are taken into account using the ideas of periodic Anderson model. The system is described by the mixture of the ground and exciting states at some finite temperature $T \neq 0$. The resulting electron potentials (self-energy) become frequency or time-dependent (*dynamical electron-electron correlations*). The most intriguing results, e.g. quasi-particle states, appear at the limit $T \rightarrow 0$.

LDA+U+SO results

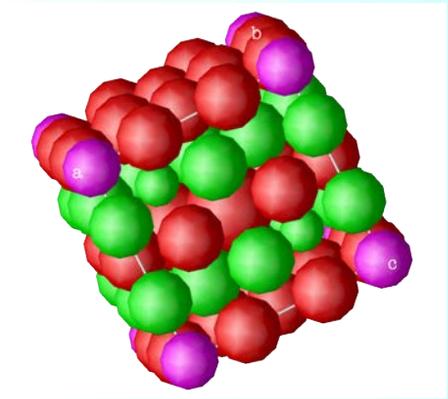
U =2.50 eV, J_H=0.48 eV, λ =0.31 eV



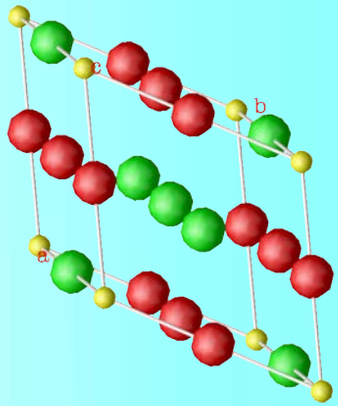


- ground state of δ- and α-Pu is **nonmagnetic**, i.e. $M_L=M_S=M_J=0$
- $f_{j=5/2}$ states are mostly occupied, $f_{j=7/2}$ – mostly unoccupied
- different degree of localization of electronic states in δ- and α-phases
- nonmagnetic ground state of pure Pu provided by **delicate balance** between competing spin-orbit and exchange interactions

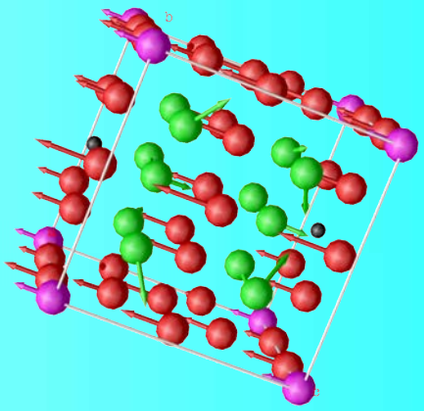
Appearance of magnetism in defect δ-Pu



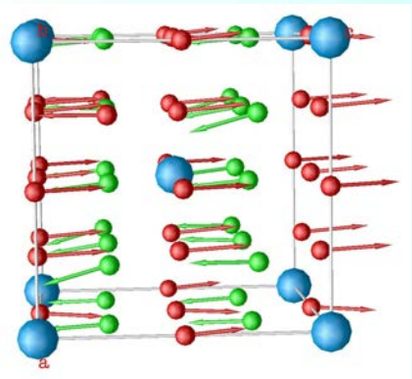
Pu as interstitial impurity.
μ_{eff}~ 0.26μ_B/atom Pu



Vacancies in Pu lattice.
μ_{eff}~ 0.28μ_B/atom Pu



Both vacancies and interstitials.
μ_{eff}~ 0.18μ_B/atom Pu



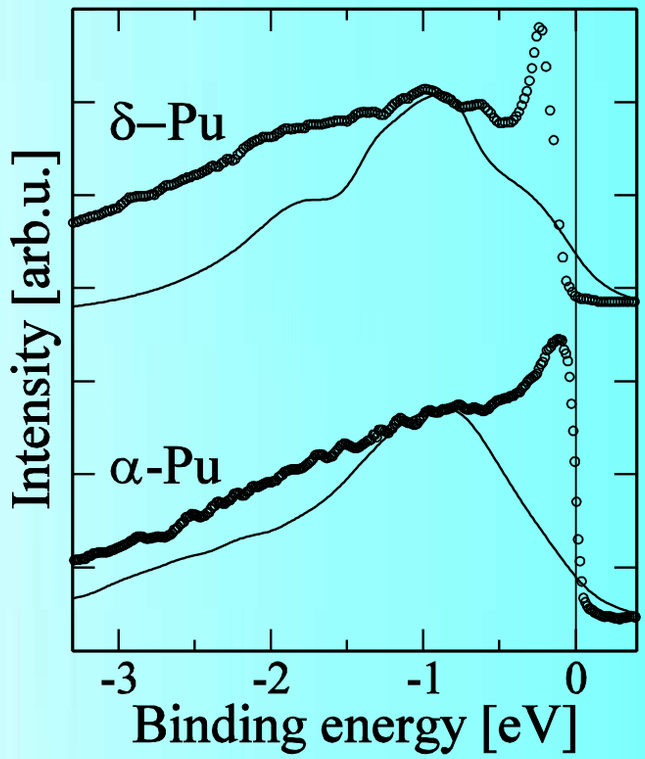
Ga substitutional impurity in Pu lattice: $Pu_{15/16}Ga_{1/16}$.
μ_{eff}~ 0.23μ_B/atom Pu

- crystal structure **defects** and (or) **impurities lead to** weak **magnetization** of Pu

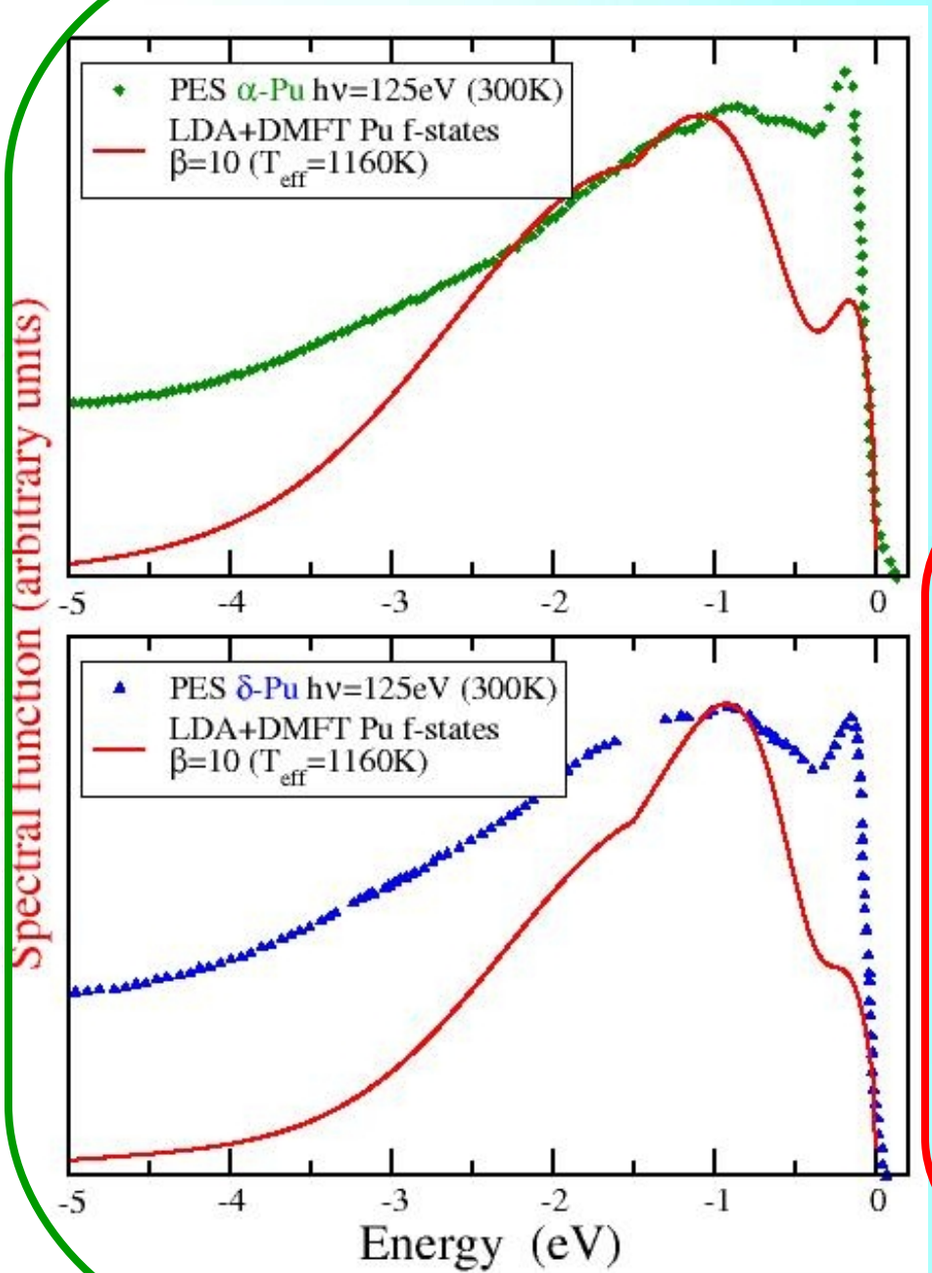
- **origin** of appearance of Pu *f*-shell magnetism **is change of occupations of** $f^{5/2}$ and $f^{7/2}$ sub-shells in comparison with occupations in pure Pu

Why LDA+DMFT is necessary?

Mostly the electronic structure and related properties of Pu are described correctly within the *LDA+U+SO* approach with the one exclusion: the presence of sharp peak of PES near the Fermi level. This peak needs dynamical fluctuations to be taken into account for proper description.



LDA+DMFT (HF-QMC) results for α- and δ-Pu



Details of calculation

- *LDA+U+SO* Hamiltonian included 14 correlated *f* spin-orbitals + all the valent *s*, *p*, *d* orbitals of Pu
- *U*=3.84 эВ was calculated and used
- impurity solver − exact Quantum Monte Carlo (QMC) method within the Hirsch-Fye scheme

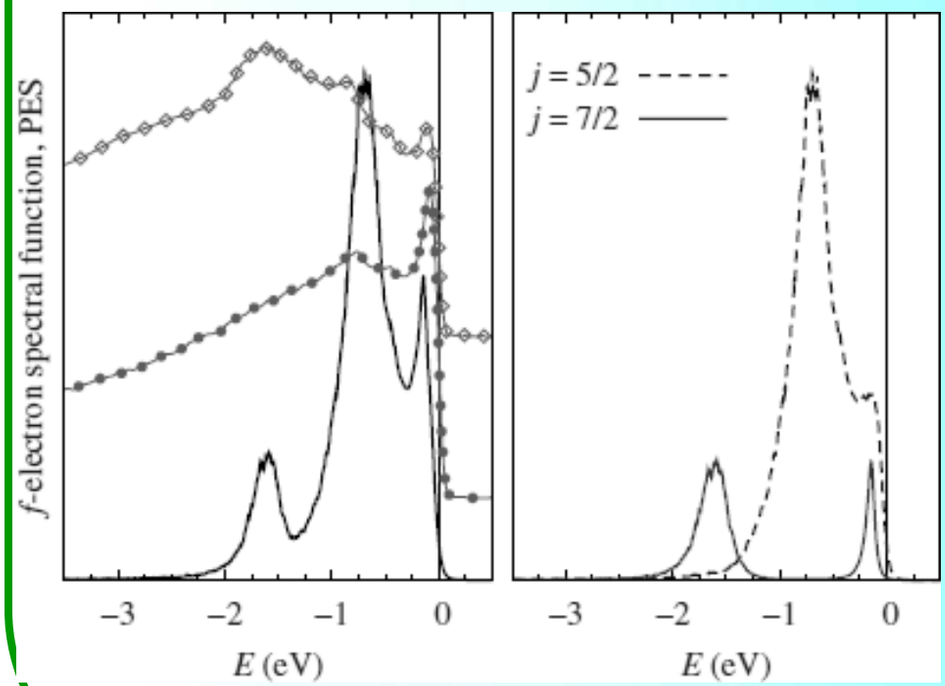
It was reproduced

- correct energy position of the lower Hubbard band
- quasi-particle peak near the Fermi level is more strongly developed in the α-phase, than in δ-phase
- average number of 5*f*-electrons due to the dynamical fluctuations was significantly decreased from its static mean-filed (*LDA+U*) value of 6 electrons to ~5.5

LDA+DMFT (CT-QMC) results for δ-Pu

The Hirsch-Fye scheme has some limitations, in particular:
- essential computer time growth considering the lower T;
- not complete Coulomb interaction are taken into account.

Another scheme for Andersen impurity model solver is
hybridization expansion continious-time QMC (CT-QMC)



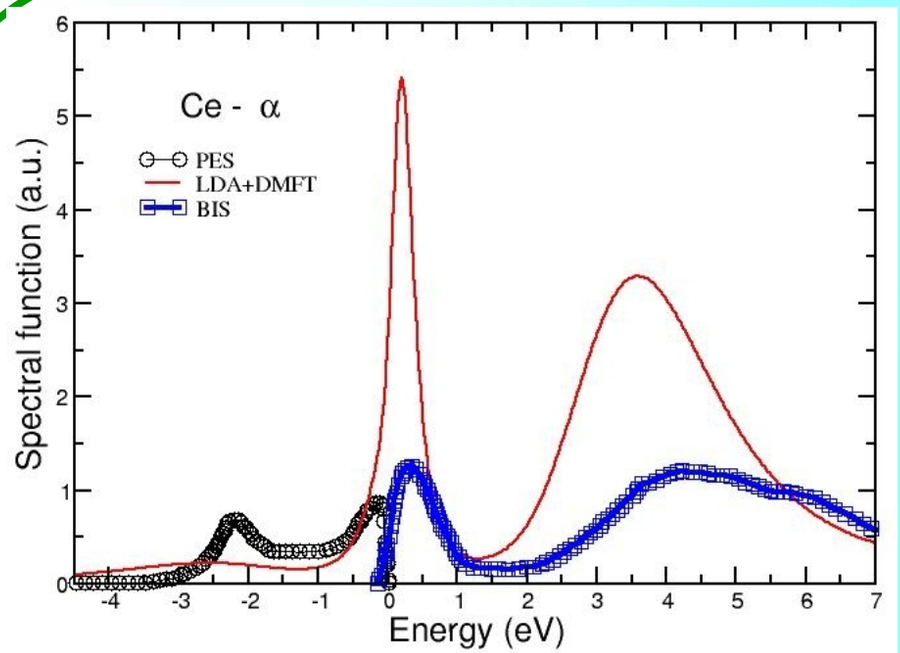
Details of calculation

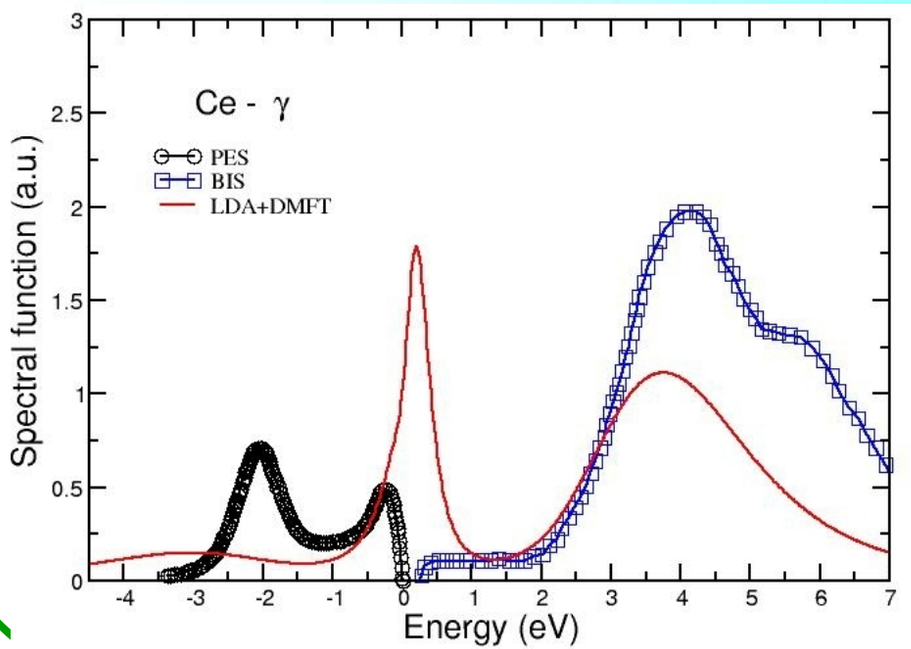
- impurity solver − weak-coupling CT-QMC
- U=4 eV, J=0.7 eV, T~ 600 K
- *full rotationally invariant* Coulomb interaction

Main results:

- the position of the quasi-particle peak near the Fermi level as well as the spin-orbit splitting of the multiplet structure well reproduce the main features of the experimental photoemission spectra
- a large contribution to the lower Hubbard bands (~−1.7 eV) comes from the high energy j=7/2 states

LDA+DMFT (CT-QMC) for α- and γ-Ce





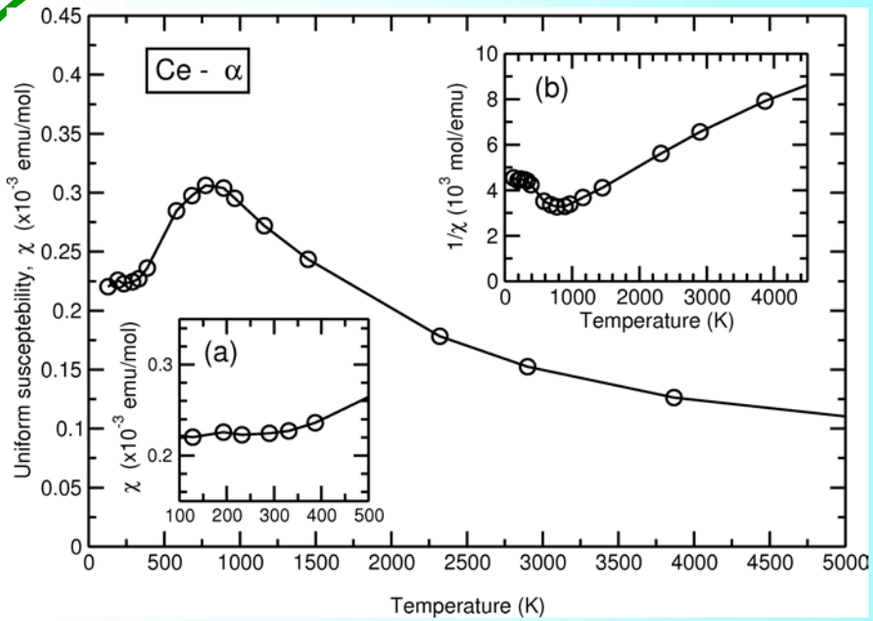
Details of calculation

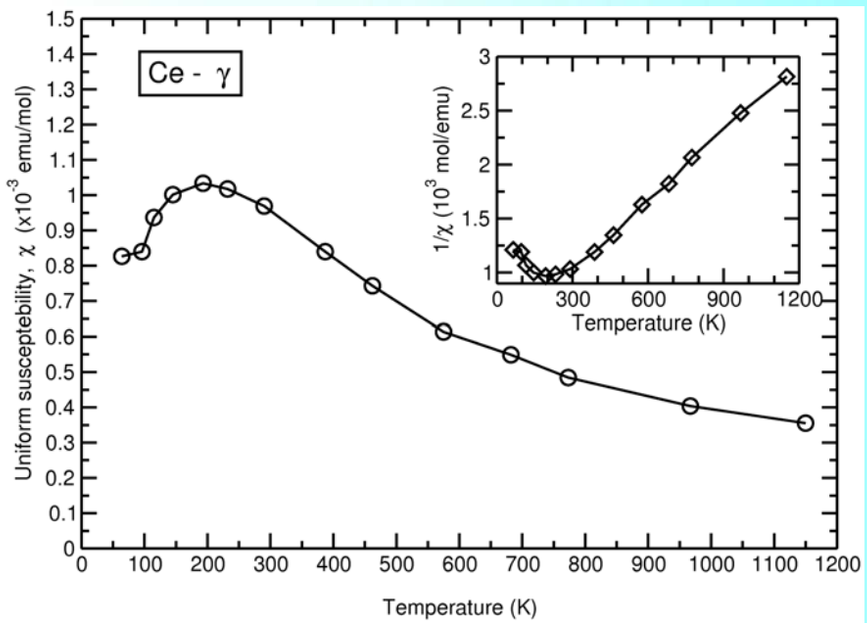
- impurity solver − CT-QMC
- U=6 eV, J=0

Main conclusions

Experimental 3-peaks structure (lower Hubbard band at ~ −3 eV, quasi-particle peak around Fermi level and upper Hubbard band at ~ +3 eV could be reproduced only in LDA+DMFT calculations.

Temperature evolution of magnetic susceptibility of α- and γ-Ce





Details of calculation

- impurity solver − CT-QMC
- for α-Ce T_{min}=129 K (β=90 эВ$^{-1}$)
- for γ-Ce T_{min}=64 K (β=180 эВ$^{-1}$)

Description of results

- at high T − Curie–Weiss behavior (localized magnetic moments)
- then transient behavior (crossover)
- at low T − plateau (screened magnetic moments, coherent Fermi liquid, Kondo regime)

Conclusions

- both phases of Ce are similar and could be described in frames of the same model with different parameters
- there is no change in the degree of localization of Ce 4*f*-electrons (**unlike Pu!**)

Conclusions

• The most modern tool for the investigation of the electronic structure and magnetic properties of actinides is ***LDA+DMFT (CT-QMC)*** method.

• It allows to describe fine peculiarities of experimental spectra and magnetic properties down to low temperatures.

Perspectives:

• Now it is the time for the description of phase diagrams of actinides.

Limitations:

• Small unit cell.

• Only pure compounds.

Computer simulation of

the phase stability at finite temperatures and
the effect of low-concentration impurities on thermodynamic and mechanical

properties of actinides

by Classical Molecular Dynamics (CMD),

including the case when inter-atomic potentials used in it are constructed
basing on the results of *ab initio* electronic structure calculations