Correlation effects in electronic structure of $PuCoGa_5$

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We report on results of the first realistic electronic structure calculations of the Pu-based $PuCoGa_5$ superconductor based on the dynamical mean field theory. We find that dynamical correlations due to the local Coulomb interaction between Pu f-electrons lead to substantial modification of the electronic structure with a narrow peak being formed in vicinity of E_F, in agreement with the experimental photoemission spectra, and in contrast with the recent calculations within the LDA+U method [1], where only static electronic correlations have been included. Both Pu and Co contribute in equal footing to the narrow peak on the density of states at the Fermi level, the Co partial density of states being prominently affected by electronic correlations on the Pu sites. The **k**-resolved spectral density is calculated and the theoretical spectral function resolved extended Van Hove singularity near E_F. This singularity may lead to enchancement of the magnetic susceptebility and favour $d-$wave superconductivity.

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The recent discovery of superconductivity in $PuCoGa_5$ [2] and $PuRhGa_5$ [3] has attracted a lot of attention to electronic structure of these Pu-based compounds. They have the same $HoCoGa_5$-type tetragonal structure as the Ce-based superconductors $CeMGa_5$ (M is transition metal) [4], however $PuCoGa_5$ has an order of magnitude higher transition temperature T_c =18.5 K, the highest T_c among known f-electron superconducting materials. Both $CeMGa_5$ and $PuMGa_5$ are unconventional superconductors [5] with the nodal $d-$ wave symmetry of superconducting gap Δ and antiferromagnetic fluctuations being a likely mechanism for their unconventional superconductivity. It has been suggested [6] that the increase of T_c in the $PuMGa_5$ compounds in comparison with $CeMGa_5$ might be due to more itinerant character of the $5f$ band in Pu.

The experimental data [2] show no evidence of a long-range magnetic structure down to temperature of 1 K, whereas the magnetic susceptibility obeys the modified Curie-Weiss law with an effective local moment 0.68 μ_B. The specific heat coefficient γ=77 mJ mol^{-1}K^{-2} [2] is slightly larger than the value observed in δ-Pu (50 mJ mol^{-1}K^{-2} [7]) indicating possible enhancement by strong dynamical spin fluctuations. The experimental photoemission spectra (PES) of $PuCoGa_5$ [8] exhibits a broad feature centered 1.2 eV below the Fermi level, which is made up of Co d- and Pu f-bands, as well as a narrow peak at the Fermi level. The latter feature is similar to narrow resonances observed in the PES of δ-Pu [9] as well as in the spectra of some Pu-based compounds [10, 11].

The electronic structure of $PuCoGa_5$ has been investigated in several papers on the basis of the local spin density approximation (LSDA) [12, 13, 14, 15]. In the non-spin-polarized band structure calculations of Refs. 12, 13 for nonmagnetic state the main f-state spectral weight is located in the vicinity of the Fermi level in contradiction with experiment. The spin polarization pushes occupied part of the f-band below the Fermi level [12, 14], with the density of states (DOS) for the antiferromagnetic phase [14] being in good agreement with the experimental PES [8]. However, the Pu total magnetic moment obtained within the LSDA is too large (around 2 μ_B) in comparison with experimentally measured μ_{eff} as well as the ordered magnetic structure in $PuCoGa_5$ predicted by the LSDA calculations has not been observed in experiment. Joyce *et al.* [8] obtained theoretical PES in a very good agreement with the experimental one using the mixed level model (MLM). In the MLM $5f$ electrons of Pu is divided in four localized and one itinerant, however the energy position of the localized states is not calculated *ab initio* but rather treated as a parameter which value is chosen to match experiment.

The strong enhancement of the specific heat coefficient γ, as well as the characteristic narrow resonance at the Fermi level, hint on possible importance of dynamical electronic correlations in $PuCoGa_5$. In δ-Pu [16] and Pu monochalcogenides [17] a good agreement between the theoretical and measured PES for non-magnetic phase (which is the ground state for these materials in accordance with the experiment) has been obtained only when dynamical correlations between f-electrons were taken into account by means of the dynamical mean-field theory (DMFT) [18] in a framework of the LDA+DMFT [19, 20] method. For $PuCoGa_5$ Shick *et al.* [1] have taken into account only *static* correlations by means of the LDA+U method. They obtained the antiferromagnetic ground state with the reduced (in comparison with the LSDA) Pu effective magnetic moment around 1 μ_B. At the same time, the density of states reported in Ref. 1 demonstrates some dis-

crepancy with the experimental PES. While the position of the broad manifold reproduced quite well, the narrow feature at E_F is absent. It seems reasonable to suggest that by analogy with δ-Pu and other Pu-based compounds an adequate description of the electronic structure of $PuCoGa_5$ requires dynamical correlations to be taken into account. It is important to notice that in the Pu-based compounds the dynamical correlations affect most profoundly the states in vicinity of the Fermi level [17], which are involved in superconductivity. It is the purpose of this Letter to present electronic structure of $PuCoGa_5$ with the dynamical electronic correlations explicitly included within the LDA+DMFT approach.

We start with the LSDA+U calculations of $PuCoGa_5$. Following Ref. 1 to allow for the antiferromagnetic ground state we double the unit cell along the $\hat{a}$ and $\hat{b}$ crystallographic axes and point magnetic moments of the nearest-neighbor Pu atoms in the Pu planes in opposite directions, the magnetic moments of Pu atoms being aligned along the crystallographic $\hat{c}$ axis. The calculations have been carried out by the full-potential linear MT-orbitals method (FPLMTO) [21] at experimental lattice parameter of $PuCoGa_5$ (a=7.845 Å, c/a=1.603 for the unit cell) with the spin-orbit coupling included in a self-consistent second-order variational procedure. We include the full matrix of on-site Coulomb interaction between Pu $5f$-electrons parametrized by the average Coulomb interactions U =3 eV and the Hunds-rule exchange J ==0.55 eV. These values of U and J are in the range of commonly accepted values for Pu. For the double counting (DC) term we have employed so-called "around mean-field" formulation of the LDA+U method [22, 23]. This version of the LDA+U method was recently successfully used to explain non-magnetic ground state of the Pu δ-phase [24]. We used previously the same values of U and J as well as the same choice of the DC in the DMFT simulations of Pu monochalcogenides [17].

The one-particle Hamiltonian $H_t(\mathbf{k})$ obtained by the converged LDA+U calculations was then orthogonalized by the Löwdin transformation [25] and used to compute the local Green's function by means of the Brillouin zone (BZ) integration

$$G(i\omega) = \sum_{\mathbf{k}} [(i\omega + \mu)\mathbf{1} - H_t(\mathbf{k}) - \Sigma^{dc}(i\omega)]^{-1}, \quad (1)$$

where $\omega = (2n+1)\pi T$ are the fermionic Matsubara frequencies for a given temperature T, μ is the chemical potential and $\Sigma^{dc}(i\omega)$ is the local self-energy with a "double counting" term subtracted. Within the DMFT scheme the local self-energy has been obtained by the solution of the many-body problem for a single quantum impurity coupled to an effective electronic "bath" through the Weiss field function [18]

$$\mathcal{G}^{-1}(i\omega) = G^{-1}(i\omega) + \Sigma^{dc}(i\omega). \quad (2)$$

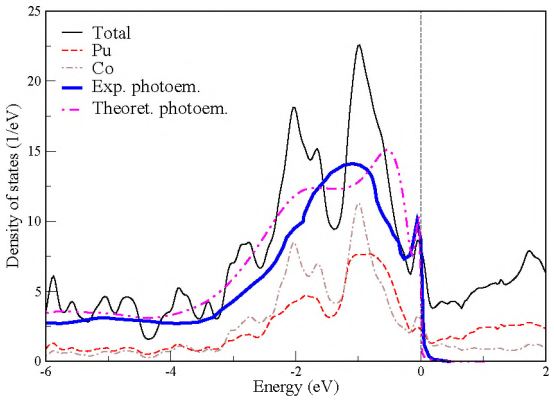

FIG. 1: The total DOS (solid line) as well as the partial DOS for Pu (dashed line) and Co (dot-dashed line) atoms obtained within the DMFT. The thick solid and dot-dashed lines are the experimental [8] and theoretical PES in arbitrary units, respectively.

As a quantum impurity solver we have employed the recently developed spin-orbit version [17] of the T-matrix and fluctuating exchange technique (SPTF) [26, 27]. In the spin-orbit SPTF the local self-energy is written as a sum of three contributions:

$$\Sigma = \Sigma^{(TH)} + \Sigma^{(TF)} + \Sigma^{(PH)}, \quad (3)$$

where $\Sigma^{(TH)}$ and $\Sigma^{(TF)}$ are the T-matrix "Hartree" and "Fock" contributions, respectively, $\Sigma^{(PH)}$ is the particle-hole contribution. $\Sigma^{(TH)}$ and $\Sigma^{(TF)}$ are obtained by substitution in the corresponding Hartree and Fock diagrams the bare Coulomb interaction with the frequency dependent T-matrix, the latter is given by summation of the ladder diagrams in the particle-particle channel. $\Sigma^{(PH)}$ is obtained by the RPA-type summation in the particle-hole channel with the bare vertex being substituted by static limit of the T-matrix [17, 27]. While being of perturbative type the spin-orbit SPTF solver has been shown to provide an adequate description of correlations in $3d$ metals [26, 27], half-metallic ferromagets [28], and some actinide systems [17].

For the double counting term in DMFT simulations we have used the static limit of the self energy [27]. For the spin-orbit SPTF quantum impurity solver we employed 10^3 Matsubara frequencies and temperature 500 K. It is important to notice that with our choice of the double counting term the Hartree-Fock contribution is already included into the LDA+U one-particle Hamiltonian, therefore making magnetization almost temperature independent. We have carried out DMTF iterations until convergence in both the chemical potential μ and

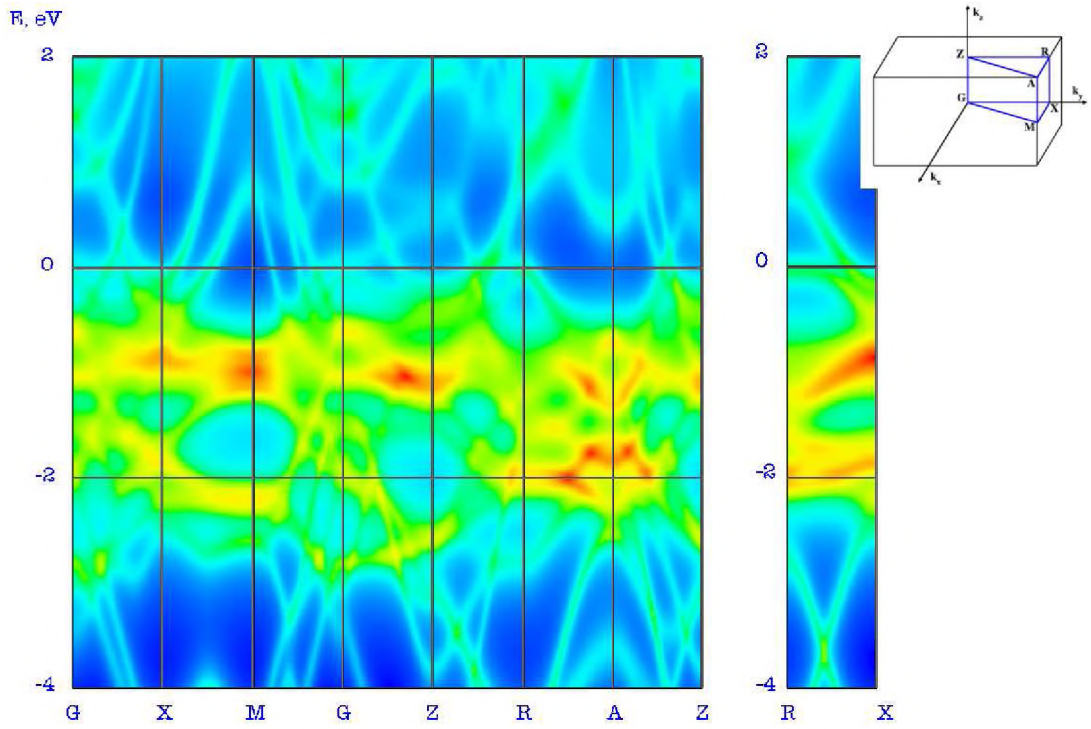

FIG. 2: The spectral function of $PuCoGa_5$. The sequence of colors in order of increasing spectral density is blue, green, yellow, and red. In the inset the BZ of $PuCoGa_5$ is shown together with our designations for the high-symmetry points.

the local self-energy was achieved. Then the Pade approximant is used [29] for analytical continuation of the local self-energy to the real axis in order to obtain the DOS $n(E) = -1/\pi \mathrm{Tr}\Im[G(E)]$ and spectral function $A(E, \mathbf{k}) = -1/\pi \mathrm{Tr}\Im[G(E, \mathbf{k})]$.

We started from the antiferromagnetic state of $PuCoGa_5$ but the self-consistent calculations converged to practically zero magnetic moments both on the Pu and Co sites. The long-range magnetic order is suppressed due to combined influence of a strong relativistic spin-orbit coupling and the local Coulomb interaction effects. The $f_{5/2}$ states of Pu in $PuCoGa_5$ are almost completely filled (the occupation number for f-band n_f=5.5) whereas the empty $f_{7/2}$ states are located around 3 eV above the Fermi level. It is this splitting that suppress the magnetism of Pu in comparison with the LSDA electronic structure. The Co 3d band is located between -2 eV and the Fermi energy.

The DMFT results for $PuCoGa_5$ DOS is shown on the Fig. 1 together with the experimental PES spectrum [8] and the theoretical PES obtained from the DMFT DOS. In order to compute the theoretical PES spectrum the calculated DOS data have been multiplied by the Fermi function corresponding to the experimental temperature of 77 K [8] and then convoluted with a Gaussian to simulate for the instrumental resolution and lifetime broadening of the core hole [8, 30]. One may see a pronounced quasiparticle peak at the Fermi level in the DMFT DOS. The theoretical PES agrees quite well with the experimental one, the shape of the feature at the Fermi level as well as relative spectral weight of the broad manifold and the resonance at E_F being reproduced very accurately. However, the manifold is somewhat wider in the theoretical PES compare with the experiment, with a peak at -0.6 eV and a shoulder at -1.8 eV.

Interestingly, while in our DMFT calculations the correlation effects have been taken into account only on the Pu sites, both the Pu f- and Co d-bands are substantially modified in comparison with the LDA+U result and they both contribute in equal footing to the narrow peak at E_F. The LSDA [15] as well as LSDA+U [1] calculations for the antiferromagnetic phase predict that the Pu f-band gives by far the dominant contribution to DOS at E_F. We have performed also the LDA+DMFT calculations with the local Coulomb interaction between Co d-electrons being included as well (with U=2 eV and J=0.9 eV), however that leads to rather minor changes in the electronic structure.

The spectral function of $PuCoGa_5$ calculated within the DMFT is displayed in Fig. 2. The maximums in spectral function around M, A and Z points correspond to both the Pu f-band and Co

d-band, contributing mainly to the manifold at energies between -2 and -1 eV. The increase of the spectral weight near the the Fermi level due to van Hove singularities (saddle points) close to R and Γ points is mainly due to the Co d-band, and in between Z and R points is due to contributions from both Co and Pu. The flat Co d band located exactly at the Fermi level is clearly seen in the spectral function along the $R-X$ direction. The extended van Hove singularity near R point together with the van Hove singularity at Γ point result in strong $\mathbf{q}$-dependence of magnetic susceptibility (cf., e.g., the "parquet" results for the two-dimensional Hubbard model [31]). This enhanced susceptibility can lead to $d-$wave superconductivity [32]. Relevance of the van Hove singularities for the superconductivity has been discussed for high-temperature cuprates [31, 33], as well as for Sr_2RuO_4 [34]. However, in comparison with these cases, the electron spectrum of $PuCoGa_5$ is a bit less anisotropic and probably can not be considered as a purely two-dimensional one even in a zeroth-order approximation (see the results for $R-X$ direction in Fig. 2).

In conclusion, we have shown that the dynamical correlation effects modify electronic structure of the $PuCoGa_5$ superconductor in essential way. We have taken the dynamical correlations into account by means of the dynamical mean-field theory using the spin-orbit T-matrix and fluctuating exchange (SPTF) approximation for the quantum impurity solver. in agreement with the experimental data, the self-consistent solution turned out to be non-magnetic. The DOS obtained by the DMFT simulations is in a good agreement with the experimental PES, with the narrow peak at the Fermi level being very well reproduced. While only Pu sites have been treated as correlated, the dynamical correlations modify the Co bands as well. On the other hand, taking into account local correlations on Co sites does not effect noticeably on the electronic structure. Both the Co and Pu bands contribute almost on equal footing to the quasiparticle resonance at E_F, in contrast with the LSDA picture, where only Pu bands contribute at DOS on the Fermi level. Theoretical spectral function demonstrates the extended Van Hove singularity near R point which is due to the Co d band. New ARPES experiments are highly desirable to investigate the energy spectrum of $PuCoGa_5$ in the vicinity of the Fermi level and check the theoretical predictions.

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