Effect of Coulomb Correlations on the Electronic Structure of $PuCoGa_5$

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We investigate the effect of strong Coulomb correlations on the electronic structure of the Pu-based superconductor $PuCoGa_5$ by employing the relativistic local spin density approximation+ Hubbard U (LSDA + U) method. The inclusion of intra-atomic Coulomb U and exchange J parameters leads to a significant reconstruction of the f states electronic structure over that given by the LSDA approach. At variance with the LSDA, the LSDA + U suggests "jj"-like coupling for the Pu $5f$ manifold.

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The recent discovery [1] of superconductivity in $PuCoGa_5$ has initiated a tremendous interest in its electronic and magnetic structure [2–4]. While f-electron based materials are well known to exhibit superconductivity, normally their superconducting T_c's do not exceed 2 K. The astonishingly high T_c of 18.5 K observed for $PuCoGa_5$ highlights the exceptional position of this material among all f-electron based superconductors [1]. The magnetic properties of $PuCoGa_5$ are particularly important for tracing down the—possibly unconventional—pairing mechanism leading to the anomalously high T_c. So far susceptibility measurements [1] provided no evidence for long-range magnetic order, but at elevated temperatures the susceptibility obeys a modified Curie-Weiss behavior with an effective moment of $0.7\mu_B$. The S-like shape of the temperature dependence of the resistivity indicates the presence of spin fluctuations induced scattering in the nonmagnetic phase. Also, the specific heat coefficient $\gamma \sim 77\ \mathrm{mJ/mol\,K^2}$ is not as high as in archetypal heavy-fermion materials, but is significantly enhanced, which could be due to the presence of strong dynamical spin fluctuations.

The electronic structure of $PuCoGa_5$ was investigated so far in several papers [2–5]. In two recent papers [2,3], relativistic electronic structure calculations on the basis of the local spin density approximation (LSDA) were reported, with a particular focus on properties of the nonmagnetic phase. Another recent investigation addresses magnetic electronic structure aspects within the LSDA framework [5]. In Ref. [4], photoemission experiments are combined with electronic structure calculations based on the mixed level model (MLM). In the MLM the five Pu $5f$ electrons are divided in four localized $5f$ electrons, treated explicitly as core states, and one delocalized $5f$ electron, which is treated using LDA band calculations. The photoemission experiments show a Pu-atom $5f$ response in the vicinity of the Fermi energy (E_F) as well as a second $5f$ related response at a binding energy of about 1.2 eV. In the MLM, the second $5f$ response is ascribed to the four localized $5f$ electrons, while the peak near the Fermi edge results from the density of states calculated for the delocalized $5f$ electron. Overall, the measured photoemission spectrum is well reproduced by the MLM.

The photoemission spectrum puts restrictions on theories of the electronic structure of $PuCoGa_5$, particularly on the $5f$ states binding energy. In the MLM the energy position of the $5f$'s treated as core states does not follow from a detailed calculation, but is adjusted by hand to match the experimental value [4]. Paramagnetic LDA band calculations [2,3] fail to reproduce the $5f$ manifold binding energy, but the LSDA approach, which takes into account spin polarization and spin-orbit coupling (SOC) together [2,5] yields a partial improvement placing a broad f band (~ 1.5 eV) at around 0.7 eV below E_F, still keeping the $5f$ manifold higher than the experimental binding energy of 1.2 eV. This indicates that the electronic structure of $PuCoGa_5$ requires an account of electron correlation effects beyond those incorporated already in the LSDA.

In this Letter we therefore apply the LSDA + U correlated energy-band approach to investigate the electronic structure of $PuCoGa_5$. The LSDA + U method starts from the LSDA total energy, which is supplemented by an additional intra-atomic Coulomb correlation term and an intra-atomic (Hund's rule) exchange interaction J term of multiband Hubbard-type minus a so-called double counting term, to subtract the electron-electron interaction already included in the LSDA (see Ref. [6] for details). Our calculations are performed using the relativistic version of the LSDA + U method, as implemented in the full-potential linearized augmented-plane-wave (FP-LAPW) scheme [6] in which the SOC is taken into account. In this implementation, the SOC is included in a self-consistent second-variational procedure (up to the $1/c^2$ order). Before considering the effect of Coulomb correlations in detail we need to make sure that this popular and widely used simplified relativistic approximation is good enough to deal with $PuCoGa_5$, in which SOC is strong.

Two of the previous computational investigations [2,3] were fully relativistic calculations based on the four-component Dirac equation. To test our computational approach, we have performed detailed comparisons with the previous fully relativistic calculations [2,3]. In our calculations we adopted the conventional von Barth-Hedin parametrization of the LSDA. Furthermore, we used 196 special k points in the irreducible part of the Brillouin zone (BZ), together with a Gaussian smearing for the k point weighting. The "muffin-tin" radii used are $R_{\mathrm{MT}} = 3.1$ a.u. for Pu, and 2.3 a.u. for both Co and Ga, while $R_{\mathrm{MT}}^{\mathrm{Pu}} \times K_{\mathrm{max}} = 10.2$, with K_{max} the cutoff for the LAPW basis. For the second-variation procedure, all the states with energy up to 3.3 Ry above the Fermi level were used, producing a basis with ~2:1 empty-to-filled states ratio in order to avoid numerical convergence problems when treating the strong Pu SOC. We used the optimized lattice constants a and c and internal Ga position z of $PuCoGa_5$ in the tetragonal $HoCoGa_5$ structure ($P4/mmm$ space group, one formula unit per cell) as given in Ref. [2]; $a = 7.842$ a.u., $c/a = 1.602$, and $z = 0.304$.

The calculated paramagnetic density of states (DOS) is shown in Fig. 1 (top) (total and atom resolved). There is a very good agreement with the DOS of Ref. [2]. The band structure in the vicinity of E_F is shown in Fig. 1 (middle panel), in almost perfect agreement with Ref. [2]. The calculated Fermi surface (FS) is shown in Fig. 1 (bottom), again in complete agreement with those of Refs. [2,3]. As for the small differences, they result from small differences in the used lattice parameters [2,5] and are connected to a very tiny balance between electrons and holes around the M point. Thus, the electronic structures are nearly identical, which proves that the simplified (up to the $1/c^2$ order) relativistic theory is capable to deal accurately with the strong SOC in $PuCoGa_5$.

Now we turn to the LSDA + U calculations. As we have already mentioned, disordered local magnetic moments are present [1] above T_c in the paramagnetic state of $PuCoGa_5$, which are not accounted for by the conventional LDA nonmagnetic theory, treating $PuCoGa_5$ as a Pauli paramagnet. In order to model the local moment paramagnet, we choose an antiferromagnetic (AFM) arrangement assuming AFM orientation of nearest-neighbor Pu atoms in the Pu planes, [7] and aligning the Pu magnetic moments along the crystallographic $\hat{c}$ axis [i.e., AFM wave vector $\mathbf{Q} = (1/2; 1/2; 0)$]. Furthermore, we adopted the experimental lattice parameters [1] and performed the calculations for several different values of the Coulomb

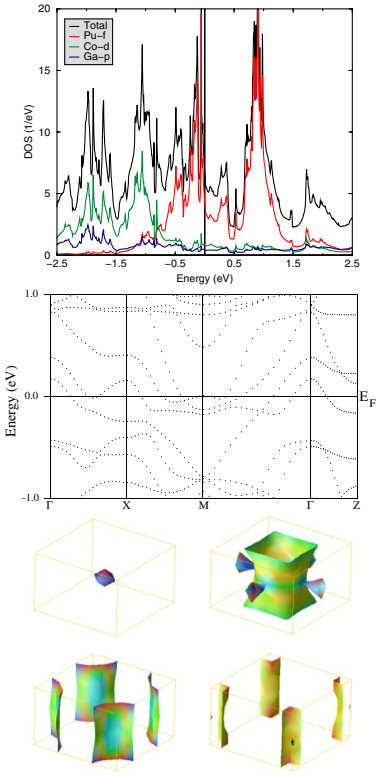

FIG. 1 (color online). $PuCoGa_5$ paramagnetic DOS (total and projected) (top); band structure in the vicinity of the E_F (middle); Fermi surface (bottom) from nonmagnetic local-density approximation calculations. The FS surface is centered at the Γ point.

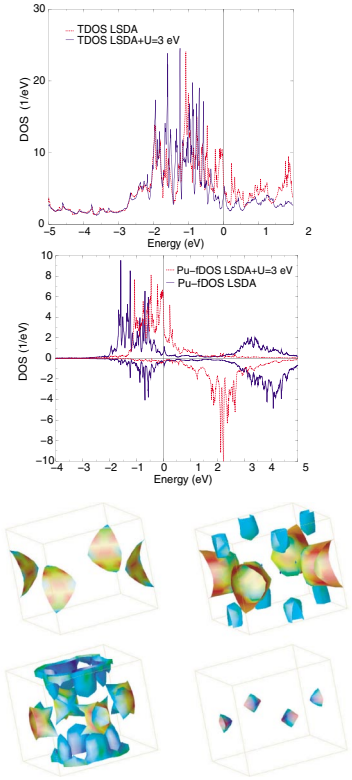

FIG. 2 (color online). The total DOS of AFM $PuCoGa_5$ as obtained from LSDA and LSDA + U ($U = 3$ eV) calculations (top); the corresponding spin-projected Pu $5f$ partial DOS (middle); the $PuCoGa_5$ FS from AFM LSDA + U ($U = 3$ eV) calculations (bottom). The FS is centered at the Γ point.

TABLE I. Ground-state magnetic properties of $PuCoGa_5$ as obtained from LSDA and LSDA + U calculations. Given are the $5f$ occupation number n_{5f}, the spin moment M_s, the orbital moment M_l, and total magnetic moment M_j (spin + orbital) per formula unit (all in μ_B), together with $C_2 = |M_l/M_j|$ and $R_{LS} = |M_l/M_s|$ ratios for the Pu atom.

U	n_{5f}	M_s	M_l	M_j	R_{LS}	C_2
LSDA	5.197	4.752	-1.871	2.881	0.39	0.65
3 eV	5.332	2.565	-1.597	0.968	0.62	1.65
4 eV	5.407	2.543	-1.520	1.023	0.60	1.49
5 eV	5.468	2.717	-1.567	1.150	0.58	1.36

U ($U = 3$, 4 and 5 eV) and intra-atomic (Hund's rule) exchange constant J ($J = 0.7$ eV). These values for U and J are in the ball park of the commonly accepted ones for Pu [8].

In Fig. 2 (top) we show the total DOS obtained for AFM $PuCoGa_5$ from LSDA + U calculations ($U = 3$ eV) in comparison with the LSDA calculated total DOS. The influence of magnetism can be seen already from the LSDA total DOS, in which the spin polarization causes a downward shift of the main peak by ~0.5 eV as well as a reduction of the paramagnetic $5f$ partial DOS at the Fermi edge [cf., Fig. 1 (top)]. Within the LSDA + U approach, the following changes can be noted: (i) a further suppression of the DOS peak in the vicinity of E_F, and (ii) an additional ~0.5 eV downward shift of the DOS weight to binding energies of ~1–2 eV. As can be seen from the f-partial DOS shown in Fig. 2 (middle), this shift is due to the modification of the Pu f states. When we compare the LSDA + U AFM DOS to the measured photoemission spectrum (Fig. 2 of Ref. [4]), it is seen that the LSDA + U approach places the $5f$ manifold at around ~1–1.5 eV in accord with experiment, and suppresses partially the $5f$ resonance at the Fermi edge. A very similar picture is obtained for $U = 4$ and 5 eV as well. These increased values of the Coulomb U do not yield any significant modification of the LSDA + U DOS shown in Fig. 2, but only slightly shift the $5f$ states down. We further note that the Coulomb U, in addition to the increased splitting of the $5f$ minority and majority spin states, causes a significant change in minority spin DOS below E_F. The physical implication and source of this DOS change is analyzed below.

The local magnetic moment behavior of $PuCoGa_5$ may have serious implications for the superconductivity as it changes the FS. The LSDA + U calculated FS for $U =$ 3 eV is shown in Fig. 2 (bottom). It consists of four double-degenerate sheets originating from the doubling of the crystallographic unit cell in the AFM calculations. This FS cannot be directly compared to the paramagnetic LDA Fermi surface shown in Fig. 1, which is computed for a different BZ. None the less, it is obvious that the LSDA + U FS displays much less two dimensionality. With the increase of the Coulomb U the FS remains stable, with changes occurring only in the second and third sheets as the Coulomb U is increased, and the FS volume, which corresponds to the f states, increases (cf., Table I). A detailed analysis of the LSDA + U Fermi surface and its implications to the superconductivity will be given elsewhere.

In Table I the calculated spin magnetic moment (M_s), orbital magnetic moment (M_l), and total magnetic moment ($M_j = M_s + M_l$) on the Pu atom are given, together with the C_2 ($= |M_l/M_j|$) and R_{LS} ($= |M_l/M_s|$) ratios. The LSDA + U yields a strong reduction of the Pu spin moment M_s—in accordance with the increased minority spin DOS—while it does not change considerably the orbital moment M_l. This is an extraordinary result since normally in LSDA + U calculations the latter is increased due to the additional (compared to LSDA) orbital polarization. As a

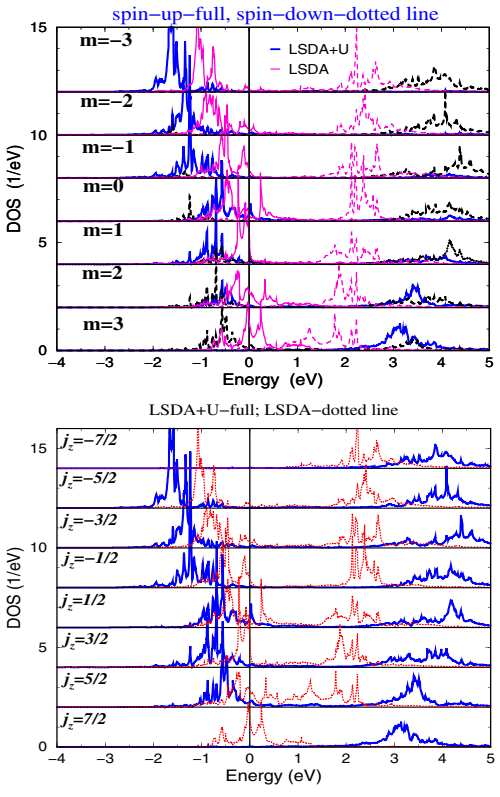

FIG. 3 (color online). $|m_l; m_s\rangle$ resolved DOS of the Pu f states from AFM LSDA and LSDA + U ($U = 3$ eV) calculations (top); the corresponding $|j_z = m_l + m_s\rangle$ resolved Pu atom f DOS (bottom).

consequence, the R_{LS} and especially C_2 ratios increase substantially by nearly a factor of 2. The source of the M_s reduction with the Coulomb U becomes evident when we compare the LSDA and LSDA + U $|m_l; m_s\rangle$ projected Pu f DOS shown in Fig. 3 (top). While in the LSDA there is almost complete spin polarization of the f states, the LSDA + U yields a stronger $\uparrow;\downarrow$ spin mixing, and flips the $|m_l = 3; m_s = \uparrow\rangle$ state into $|m_l = 3; m_s = \downarrow\rangle$, which contributes substantially to the M_s reduction [9] while keeping the M_l nearly constant.

The difference between LSDA and LSDA + U becomes even more evident when we compare the $|j_z\rangle = |m_l + m_s\rangle$ projected Pu f DOS, [10], which is shown in Fig. 3 (bottom). While the LSDA fills the occupied f states starting from $j_z = -5/2$ up to $j_z = 7/2$, the LSDA + U occupies the states starting from $j_z = -5/2$ to $j_z = 5/2$ only and splits away the subsets of the states with $j_z = -7/2$ and up to $j_z = 7/2$. Again, the main difference appears in the $|j_z = 7/2\rangle$ subset, having $|m_l = 3; m_s = \uparrow\rangle$ character, which is partially filled in the LSDA. The LSDA + U empties the $|m_l = 3; m_s = \uparrow\rangle$ and occupies the $|m_l = 3; m_s = \downarrow\rangle$ state, which contributes to the $|j_z = 5/2\rangle$ subset.

The LSDA + U picture shown in Fig. 3 can be qualitatively interpreted as "anomalous" Zeeman-like split $E_{jlm} = E_j - Bg_j j_z$, "lower" $j = 5/2$ (occupied), and "higher" $j = 7/2$ (empty) manifolds in the presence of an effective magnetic (exchange-correlation) field B. Such type of splitting occurs when the SOC is much larger than the effective magnetic field B. Its appearance is significant, because in the LSDA + U interaction model, the spin-$\uparrow;\downarrow$ contributions entering the LSDA + U effective potential lead to an enhancement of the effective spin-orbit coupling [6]. We emphasize here that both the LSDA and LSDA + U models are not based on any kind of atomic coupling scheme (e.g., LS or jj coupling), rather they determine the set of single-particle orbitals that minimize variationally the total energy. For both the LSDA and LSDA + U models the variationally optimized single-particle orbitals can be interpreted as the set that forms a lowest-energy Slater determinant. Within the LSDA + U, this leads to a ground-state configuration which corresponds in a natural way to the jj-atomiclike coupled Slater determinant formed of the $j = 5/2$, $j_z = -5/2, \cdots, 5/2$ orbitals (the same picture is found to hold for $U = 4$, 5 eV as well). Within the LSDA, however, the $j = 7/2$, $j_z = 7/2$ orbital is partly occupied, which does not correspond to jj-atomiclike coupling. Recently, the importance of jj coupling for α Pu and δ Pu has been concluded from spectroscopic evidence [11]. The use of a jj-coupling scheme for analyzing the electronic structure of $PuCoGa_5$ has also been intuitively suggested in Ref. [3].

To summarize, taking into account strong Coulomb correlations within the framework of the relativistic LSDA + U energy-band theory leads to a significant reconstruction of the Pu $5f$ states manifold. As an unexpected consequence, our calculations show that the calculated Pu atomic spin moment becomes reduced, while the orbital moment is not affected as much. The mean-field treatment of the Coulomb U and exchange J interactions suggest that the Pu $5f$ states retain some atomiclike features in $PuCoGa_5$ in spite of a fair amount of hybridization. It also suggests, unlike the outcome of LSDA calculations, a jj-like coupled, Pu ground-state configuration in $PuCoGa_5$.

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