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Fermiology of $PuCoGa_5$ and of related Pu-115 compounds

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Abstract

We report computational investigations of the electronic structures of the superconducting Pu-compounds $PuCoGa_5$ as well as of the non-superconducting compounds $PuFeGa_5$ and $PuNiGa_5$. To capture the localization behavior of the Pu 5f electrons, we apply two computational approaches, which are both rooted in the density-functional theory: the local spin-density approximation (LSDA) and the around mean field (AMF) LSDA + U approach. The latter is applicable to moderately localized 5f electrons while the former is applicable to delocalized 5f electrons. Our LSDA calculations show that the Fermi surfaces of the three Pu-115 compounds are sensitive to the amount of band filling, i.e., the number of electrons of the 3d element. Precisely at the electron filling corresponding to $PuCoGa_5$ the Fermi surface has a particularly two-dimensional shape. AMF–LSDA+U calculations (with a Coulomb U of about 3 eV and exchange J of 0.6 eV) lead to a non-magnetic ground state for $PuCoGa_5$, in which the 5f states are shifted to a higher binding energy, in better agreement with photoemission data. The Fermi surface of $PuCoGa_5$ computed with the AMF–LSDA+U approach is nonetheless rather two-dimensional and similar to the LSDA Fermi surface. The AMF–LSDA+U approach with a Coulomb U of ≈ 3 eV would thus predict an electronic structure for $PuCoGa_5$ in accord with several experimental data.

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1. Introduction

Plutonium-based materials have for many years been studied in connection to their usage in nuclear energy applications. Through the discovery of superconductivity [1] at a very high transition temperature of $T_c = 18.5$ K in the Pu material $PuCoGa_5$ the focus on Pu has completely changed. Pu materials have recently emerged as an important topic in fundamental science and a tremendous research activity has developed as of late (see, e.g., [2–14]).

The unexpected discovery of superconductivity in $PuCoGa_5$ poses a major challenge to our understanding of superconductivity in correlated materials. To some extent the situation is comparable to the one that emerged after the discovery of superconductivity in the high-T_c copper oxides. Likewise, there was not a single Pu-based material known to be a superconductor prior to the discovery of $PuCoGa_5$, and in addition, a T_c of 18.5 K can be regarded as very high, since it is a rarity to find a material with a T_c above 2 K within the group of actinide-based superconductors. On top of this, it was recently reported that the superconductivity occurring in $PuCoGa_5$ and in the isoelectronic compound $PuRhGa_5$ is of the unconventional, spin-singlet d-wave type [10,11]. Perhaps by a matter of plain coincidence, but it is the same type of unconventional superconductivity that has been discovered for the high-T_c copper oxides [15].

The recent discoveries seem to indicate that an unconventional mechanism is responsible for the Cooper pair formation.

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As has been discussed for the high-T_c's it could be that spin-fluctuations act as the mediators of the pair formation. For both the high-T_c's and the Pu-based superconductors this is a scientifically challenging, fundamental issue. Obviously, the Pu-superconductors are a extremely interesting group of materials, displaying – on the one hand – properties of heavy-fermion superconductors (with T_c's ≤ 2 K) and on the other hand similarities to the high-T_c materials ($T_c \approx 100$ K).

The electronic structures of the Pu-115 compounds and how these relate to the superconductivity are ill-understood. The initial investigations indicated the presence of a magnetic Pu^{3+} ion ($5f^5$ configuration) [1,2]. This would indicate a clear proximity to a magnetic phase, and emphasize the importance of the occurrence of spin-fluctuations, even when long-range magnetic order does not develop above 18 K. Recently, in drawing an analogy between the heavy-fermion superconductors, the Pu-115 materials and the high-T_c superconductors, antiferromagnetic spin-fluctuations were proposed as the unconventional pairing mechanism [10]. Also, *ab initio* calculations [3] predicted antiferromagnetic order on the Pu atoms (at $T = 0$), and an analysis of the measured temperature-dependent resistivity curve indicated the presence of spin-fluctuations [8]. Recent measurements [16] on newer $PuCoGa_5$ samples indicated however that the magnetic susceptibility might be considerably smaller than the one obtained in the initial measurements [1]. These newer measurements put constraints on models for an unconventional, magnetic pairing mechanism. It could therefore still be a long way to go before a clear and coherent picture of the unconventional superconductivity in these materials can be established.

We report here electronic structure calculations, focusing mainly on $PuCoGa_5$. We also investigated the related compounds $PuFeGa_5$ and $PuNiGa_5$. These related Pu-115 compounds do not exhibit superconductivity and, in addition, are found to be non-magnetic materials [17]. This means that – as a function of the total number of valence electrons – superconductivity only occurs in a narrow region around the electron count corresponding to $PuCoGa_5$ [17]. We performed LSDA-based calculations of the electronic structures of these three neighboring Pu-115 compounds and investigated the changes in the Fermi surfaces as a function of electron count. As the 5f localization transition in the actinide series occurs between the elements Pu and Am, a tendency to 5f localization can be expected for the Pu-115 compounds. To capture this behavior, we have performed AMF–LSDA+U calculations for $PuCoGa_5$. We investigate here the effect of the additional Coulomb U on the Fermi surface of $PuCoGa_5$.

2. Computational approaches

We have applied, as a basic framework, the density functional theory (DFT) together with various different models to describe the electron's exchange-correlation. Specifically, we have used the local-spin-density approximation (LSDA) as well as the generalized gradient approximation (GGA) [18]. To capture strong Coulomb correlations beyond those contained already in the LSDA or GGA approximation, we have used the LSDA+U approach [19], in which the around mean field (AMF) form of the double counting [20] has been adopted. Our calculations have been carried out using two relativistic band-structure methods, the full-potential linear muffin-tin orbital (FP-LMTO) method [21] and the full-potential linearized augmented plane wave (FP-LAPW) method [22]. For further computational details, we refer to recent papers on electronic structure calculations of actinide compounds [9,23,24]. For the lattice parameters of the Pu-115 compounds in the $HoCoGa_5$ structure, we have adopted the experimentally determined lattice constants [17].

3. Calculated electronic structures and Fermi surfaces

First we consider here the Fermi surfaces of $PuFeGa_5$ and $PuNiGa_5$ computed using the GGA approach. The calculated Fermi surface of $PuCoGa_5$ has been published before [3,4,7,9], therefore we do not show it here again. We mention that the Fermi surface of non-magnetic $PuCoGa_5$ consists of four sheets, three of which are nearly cylindrical. The Fermi surface of $PuCoGa_5$ exhibits thus a high degree of two-dimensionality [3]. Recently, the bare, non-interacting susceptibility $\chi(\mathbf{q})$ of $PuCoGa_5$ was computed [25]. These calculations detailed that there is a substantial amount of nesting behavior of the two-dimensional FS, particularly for the wavevector $\mathbf{q} = (1/2, 1/2, 0)$. For $PuFeGa_5$ we also obtain four Fermi surface sheets, which are shown in Fig. 1. The Fermi surface of $PuNiGa_5$ is computed to consists of five Fermi surface sheets; for reasons of space restrictions, we do not show these here. Comparing first the Fermi surface of $PuFeGa_5$ with that of $PuCoGa_5$, we can immediately see how the Fermi surface sheets change with the transition metal. The three sheets (i.e., sheets 2–4) which exhibit a nearly two-dimensional shape for $PuCoGa_5$ are much less two-dimensional for $PuFeGa_5$. Thus, it can be anticipated that $PuCoGa_5$ exhibits a much larger nesting behavior than $PuFeGa_5$. The Fermi surface sheets of $PuNiGa_5$ (not shown) exhibit also a much less two-dimensional shape. Altogether, the Fermi surfaces of both $PuFeGa_5$ and $PuNiGa_5$ display much less two-dimensionality when compared to $PuCoGa_5$ and it does not exhibit a clear nesting behavior as there exists for the concentric cylindrical Fermi surface sheets of $PuCoGa_5$ [7].

These GGA calculations are applicable when the 5f electrons are to a large extent delocalized. Precisely the degree of localization of the 5f electrons is an important issue for elemental Pu and Pu-compounds. Recent photoemission experiments [5] on $PuCoGa_5$ have emphasized a appreciable degree of 5f localization, which was inferred from a 5f photoemission response at a binding energy of about 1 eV, in addition to a 5f response near the Fermi energy (E_F). These experiments thus stress the importance of Coulomb correlations within the Pu 5f shell, which were taken into account in recent LSDA + U calculations [9]. In those LSDA + U calculations, the so-called fully localized limit (FLL) of the double counting term was applied; these FLL–LSDA+U calculations showed that the spin-magnetic moment on Pu is considerably

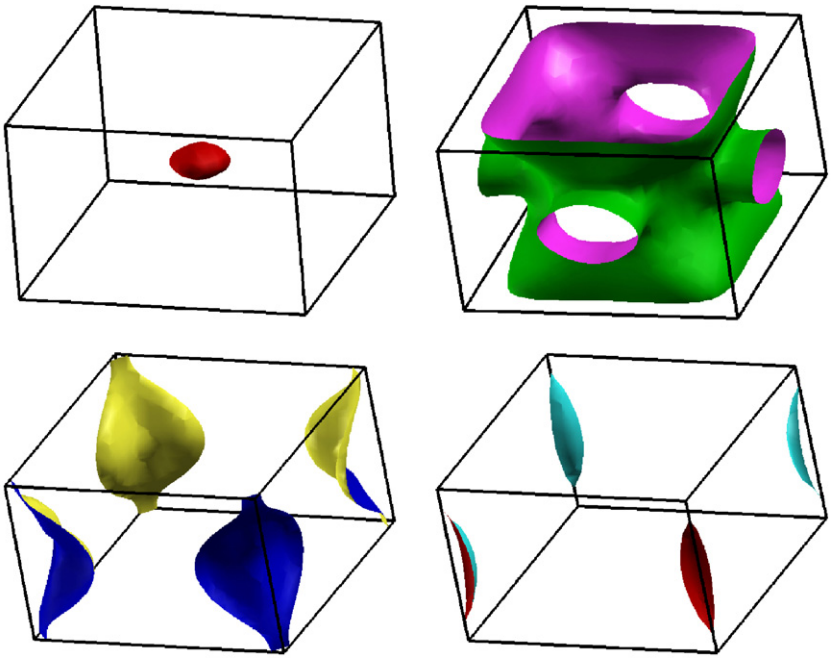

Fig. 1. Calculated GGA Fermi surface sheets of non-magnetic $PuFeGa_5$.

reduced for a U of about 3–4 eV. The selfconsistent calculations were performed for the minimal-total energy antiferromagnetic order (see [3]). Since the antiferromagnetic calculations require a double unit cell, the computed FLL–LSDA+U Fermi surface could not directly be compared with the LSDA or GGA non-magnetic Fermi surface, computed for the single unit cell. Therefore, it could not be investigated whether the LSDA+U Fermi surface also exhibits a two-dimensional shape or not.

Here we have applied the AMF–LSDA+U approach to $PuCoGa_5$. In contrast to the FLL–LSDA+U, the AMF–LSDA+U predicts a non-magnetic groundstate for $PuCoGa_5$. The energy bands of $PuCoGa_5$ calculated with the AMF–LSDA+U approach are shown in Fig. 2. The amount of 'f' character in the bands is depicted by the fatness of the bands. We note that an appreciable amount of 'f' character can be observed for the energy bands placed about 1 eV below E_F. Also, the bands at E_F contain some 'f' character, but not as much as given by LSDA calculations [3]. Both aspects are in qualitative agreement with the recent photoemission experiments [5].

Other recent measurements on $PuRhGa_5$ revealed a large anisotropy of the upper critical field H_{c2} [12], which was predicted earlier on account of the two-dimensional, LSDA Fermi surface [3,7]. Thus, it seems that the two-dimensionality of the Fermi surface, as well as the 5f positions obtained from photoelectron spectroscopy have to be comprised in the electronic structure. While not apparent at first sight from the energy bands shown in Fig. 2, the AMF–LSDA+U Fermi surface of $PuCoGa_5$ turns out to be very two-dimensional (see Fig. 3). Unexpectedly, the AMF–LSDA+U Fermi surface is very similar to the LSDA Fermi surface!

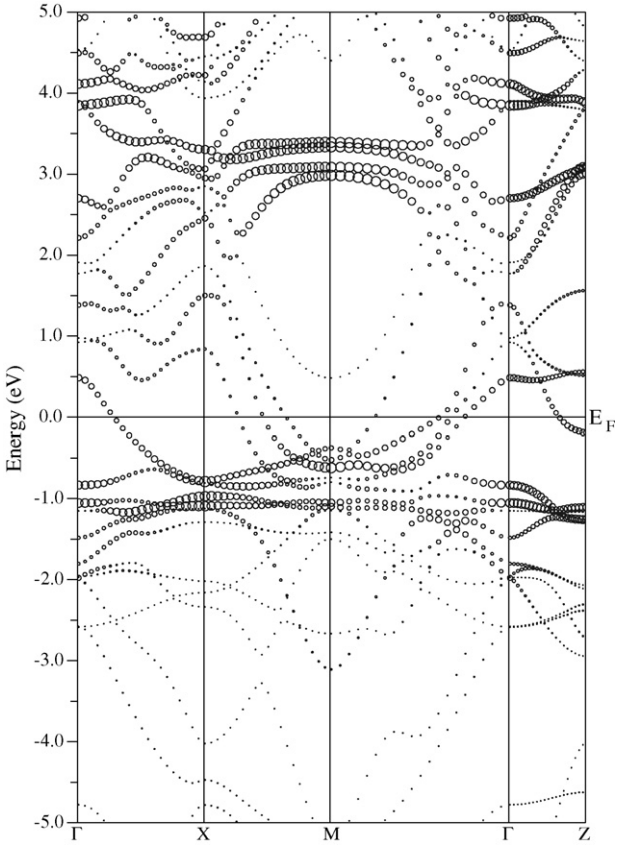

Fig. 2. The AMF–LSDA+U energy bands of $PuCoGa_5$, calculated with $U = 3$ eV and $J = 0.6$ eV. The fatness of the bands indicates the amount of 'f' character in the band.

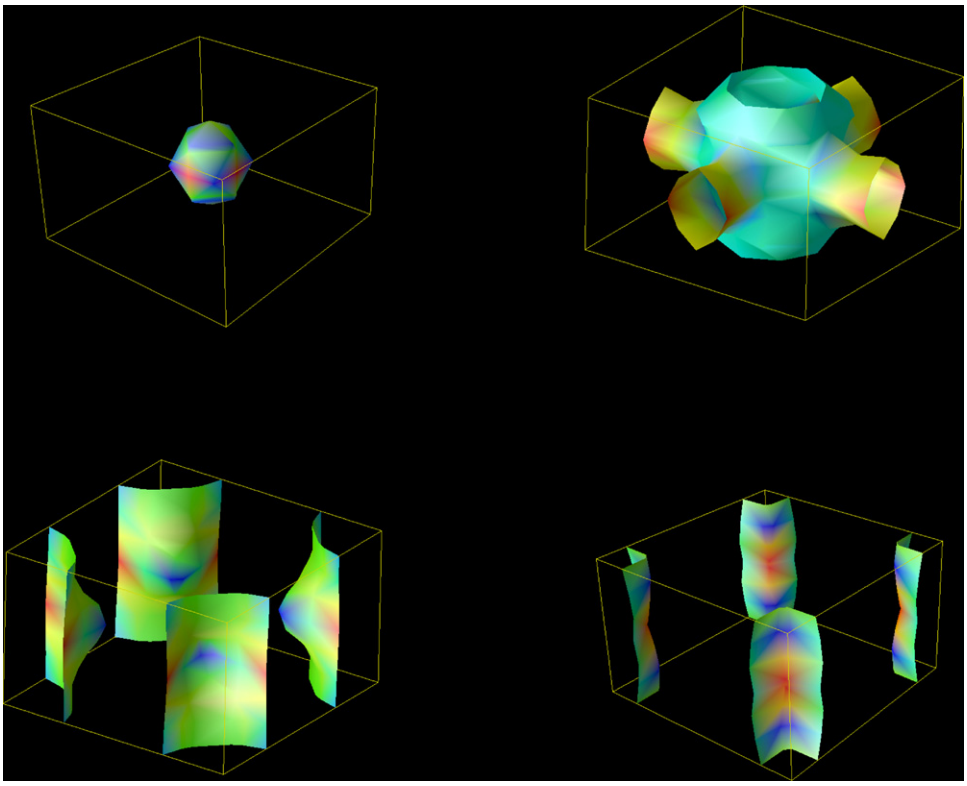

Fig. 3. The Fermi surface of $PuCoGa_5$, computed with the AMF–LSDA+U approach.

4. Discussion and conclusions

The low-temperature properties of the three $PuMGa_5$ (M = Fe, Co, Ni) compounds are quite different. Our GGA calculations show that the Fermi surfaces of both $PuFeGa_5$ and $PuNiGa_5$ exhibit much less a two-dimensional shape than that of $PuCoGa_5$. The larger degree of Fermi surface nesting in $PuCoGa_5$ could play a role for the singular occurrence of superconductivity in the Co allotrope. Surprisingly, the Fermi surface computed with the AMF–LSDA+U method is also very two-dimensional and similar to the LSDA/GGA Fermi surface. Moreover, in the AMF–LSDA+U calculations the positions of the 5f states at around 1 eV below E_F are in qualitative agreement with the 5f binding energies deduced from photoemission experiments [5]. Since the 5f states in the AMF–LSDA+U are moderately localized, multiplet excitations can be expected to occur. Their calculation will be the subject of future investigations. The AMF–LSDA+U approach predicts, in addition, a non-magnetic groundstate for $PuCoGa_5$, for a 5f occupation number of about 5.5. The disappearance of the magnetism on Pu is completely due to the AMF double counting term, leading to a filling of the 5f subshell corresponding more to j–j coupling, and obviously does not result from dynamical fluctuations. The absence of magnetism in $PuCoGa_5$, as given by the AMF–LSDA+U calculations, might be in agreement with measurements on newer samples indicating a small magnetic susceptibility [16]. Altogether, the AMF–LSDA+U approach, with $U \approx 3$ eV and $J = 0.6$ eV, provides an electronic structure for $PuCoGa_5$ which is in consistent accord with available experimental data.

Recently, the phonon spectrum of $PuCoGa_5$ has been measured [13] and has been compared to calculated phonon spectra [26]. The best agreement with experiment was obtained for a Coulomb U of about 3 eV, thus suggesting that this value of U would describe the electronic structure of $PuCoGa_5$ best [13]. We mention that the LSDA+U calculations of Ref. [26] were done using the FLL double counting term, however, neglected the spin–orbit interaction, and furthermore had full spin-polarization of the Pu atom. Both the spin–orbit splitting of Pu and the exchange splitting can modify the energy bands on an energy scale of several eV and are not small compared to the Coulomb U. Nonetheless, it appears that consensus is developing for a 5f Coulomb correlation value of around 3 eV for $PuCoGa_5$.

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