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Density-functional electronic structure of $PuCoGa_5$

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Density-functional electronic-structure calculations for $PuCoGa_5$ are performed to address the possibility of magnetic interactions in this high-temperature superconductor. Within an itinerant $5f$-electron picture, cohesion and crystallographic parameters compares favorably with experiment, whereas only when spin and orbital interactions are accounted for the calculated electronic density of states agrees with photoemission spectra. This fact suggests that spin and orbital correlations are important for a correct description of the $PuCoGa_5$ electronic structure and may play a role in an unconventional mechanism for superconductivity.

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I. INTRODUCTION

Two years ago, the first superconducting plutonium-based compound was discovered.[1] Because of the very high critical temperature ($T_c = 18.5$ K) it was argued[1] that the underlying mechanism for the superconductivity was unconventional and consistent with models of magnetically mediated superconductivity.[2] Arguably, the superconducting properties of this compound results from plutonium's anomalous electronic properties. Consequently, several theoretical investigations have addressed the electronic structure of $PuCoGa_5$, most of which were relying on the first-principles density-functional (DF) framework.[3–5] Also a model, originally developed for the treatment of δ-Pu,[6] namely the so-called mixed-level-model (MLM), was applied for the electronic structure of $PuCoGa_5$.[7] In the first-principles studies[3–5] a fully itinerant nature of the $5f$ electrons was assumed, which was corroborated by the facts that this approach yields about five $5f$ valence electrons[4] (consistent with that of the Pu^{3+} ion) and that the crystal geometry and dimensions were very well reproduced.[3] Joyce *et al.*[7] argued, however, that the $5f$ electrons in $PuCoGa_5$ are similar to that of δ-Pu and should be treated within the MLM because traditional DF calculations can not reproduce the photoemission spectra (PES) for $PuCoGa_5$, whereas a calculation within the MLM can.[7]

Opahle and Oppeneer,[3] on the other hand, performed spin-polarized calculations, assuming ferro and antiferromagnetic configurations, which were shown to have lower total energies (0.02 Ry) than the nonmagnetic configuration. Nevertheless, both the magnetic and nonmagnetic treatment[3] of $PuCoGa_5$ seemed reasonable and no preference for either one was provided.[3] Experimentally, $PuCoGa_5$ shows a Curie-Weiss (antiferromagnetic) behavior of its magnetic susceptibility at elevated temperatures,[1] indicative of a local-moment behavior close to that expected for Pu^{3+}.

The above described theoretical and experimental studies give a confusing picture of the $5f$ electrons in $PuCoGa_5$, which of course is very important for the understanding of the superconducting mechanism.[4] The DF calculations are consistent with itinerant $5f$ electrons, whereas the MLM indicates that the $5f$ manifold split into 4 localized and 1 delocalized state. The latter notion is supported by the PES, under the assumption that there are no magnetic interactions present in $PuCoGa_5$. The evidence from magnetic susceptibility[1] and the fact that Pu^{3+} is a magnetic ion suggest, however, that there is no reason to *a priori* rule out such interactions. In the present paper we use first-principles electronic-structure results to address the possibility of magnetism in $PuCoGa_5$. Section II deals with details of our calculations, Sec. III present the results, and finally in Sec. IV we conclude.

II. COMPUTATIONAL DETAILS

The electronic structure and total energy are obtained from an all electron full-potential linear muffin-tin orbitals method (FPLMTO). This implementation has been used extensively and successfully for transition and actinide metals[8] and allow for spin/orbital polarization and spin-orbit coupling in the customary ways.[9–11] The "full potential" refers to the use of nonspherical contributions to the electron charge density and potential. This is accomplished by expanding these in cubic harmonics inside nonoverlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for Pu's semicore $6s$, $6p$, and valence $7s$, $7p$, $6d$, and $5f$ states, these pairs are different. For the Co and Ga atoms, $4s$, $4p$, and $3d$ states comprise the valence. Spherical harmonic expansions are carried out through $l_{\max} = 6$ for the bases, potential, and charge density. For the electron exchange and correlation energy functional, the generalized gradient approximation is adopted.[12]

The crystal structure of $PuCoGa_5$ is tetragonal and of the $HoCoGa_5$ type,[1] with a c/a axial ratio and an internal atomic coordinate z, not bound by the symmetry. The c/a and the z parameter are both relaxed to ensure the minimum total energy of the compound. All calculations are performed for a 14 atom super cell which can accommodate the antiferromagnetic configuration. The sampling of the irreducible Brillouin zone is done using the special k-point method[13] with up to 128 k points. To each energy eigenvalue a Gaussian is associated with 20 mRy width to speed up convergency. For calculations of the electronic density of states (DOS) the sampling of the k points are accomplished by the tetrahedron method.[14] When compared to photoemission, the DOS is convoluted with a lifetime broadening[16] and for the raw DOS a Gaussian broadening with a 3 mRy width is applied.

TABLE I. Theoretical (antiferromagnetic) and experimental lattice constant a(Å), axial ratio c/a, internal atomic coordinate z, and bulk modulus B(GPa).

Quantity	Present theory	Theory[a]	Experiment[b]
a	4.259	4.150	4.232
c/a	1.613	1.602	1.603
z	0.310	0.304	0.312
B	87		

[a] Opahle and P. M. Oppeneer (Ref. 3).

[b] J. L. Sarrao *et al.* (Ref. 1).

III. RESULTS

From total-energy calculations several bulk properties of $PuCoGa_5$ can be obtained and some of them are listed in Table I. In the table we compare results from our antiferromagnetic treatment of $PuCoGa_5$ with results, from magnetic theory by Opahle and Oppeneer,[3] and experimental data from Sarrao *et al.*[1] Notice that the cohesion is very well reproduced by the assumption of itinerant $5f$ electrons, as pointed out by Opahle and Oppeneer.[3] Their calculated lattice constant is somewhat smaller than ours and the exact reason for this discrepancy is unclear. It has been shown, however, that the numerical implementation of spin-orbit coupling in electronic-structure methods can give rise to slight differences in calculated lattice constants in the actinide metals.[15]

Compared to the experimental data, the lattice constant, axial ratio, and the internal atomic coordinate, all agree within about 0.6%. The calculated bulk modulus (87 GPa) is relatively small and somewhat larger than that of α-Pu (~50 GPa) but no experimental bulk modulus is known that can be compared with. For a spin-restricted calculation, the lattice constant and the axial ratio compares somewhat less favorably with experiment, with a being large (4.271 Å) and c/a small (1.58). In a model calculation, assuming the $5f$ electrons to be localized as part of the Pu core, a is much too large (4.37 Å) and in substantial disagreement with experiment.

The attained agreement with experiment, when treating the $5f$ electrons as itinerant, gives us confidence that this procedure is justified for $PuCoGa_5$. Although the antiferromagnetic calculation has lower total energy (0.035 Ry) and give better crystallographic parameters, the nonmagnetic treatment seems to be quite reasonable as well. Another sensitive test to the theory is to compare with recent photoemission data by Joyce *et al.*[7] In Fig. 1 this comparison is made for the nonmagnetic calculation. The calculated (raw) DOS has a sharp peak shifted about 0.2 eV below the Fermi level (E_F). This does not agree with the PES, which indicate a peak pinned right at the E_F. More seriously, the measured broad manifold at about −1.2 eV is not at all reproduced by the nonmagnetic theory. Overall, an itinerant GGA calculation, as noticed by Joyce *et al.*,[7] shows poor agreement with the PES. Next, we plot in Fig. 2 the same quantities as in Fig. 1 but with results from antiferromagnetic calculations. Clearly, there is a smaller peak in the DOS, very close to the E_F, which nicely reproduce the behavior of the PES. Actually, from the Fermi level to about −1.0 eV, theory and experiment agree exceptionally well and better than that of the MLM model.[7] The agreement is also good at lower binding energies and for spectra below −3 eV, the results are more or less independent on model (nonmagnetic, antiferromagnetic, or MLM).

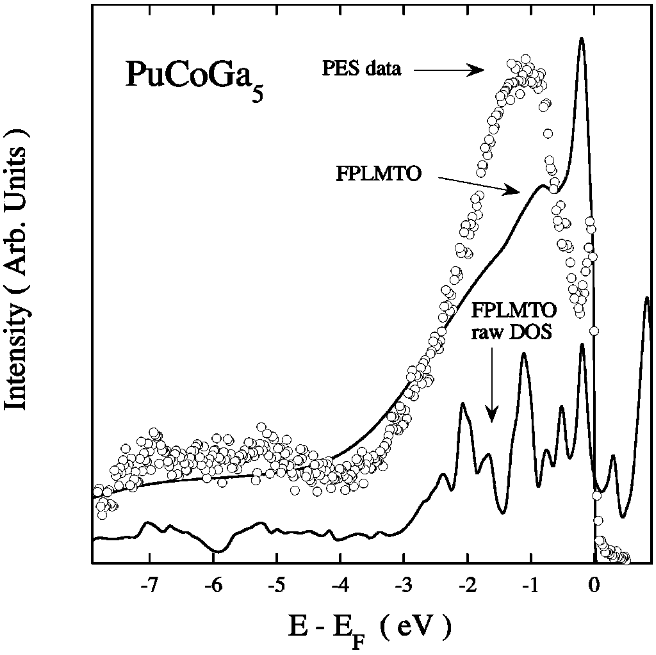

FIG. 1. PES from Joyce *et al.* (Ref. 7) together with DOS (raw DOS) and lifetime broadened DOS, obtained from a spin-restricted calculation.

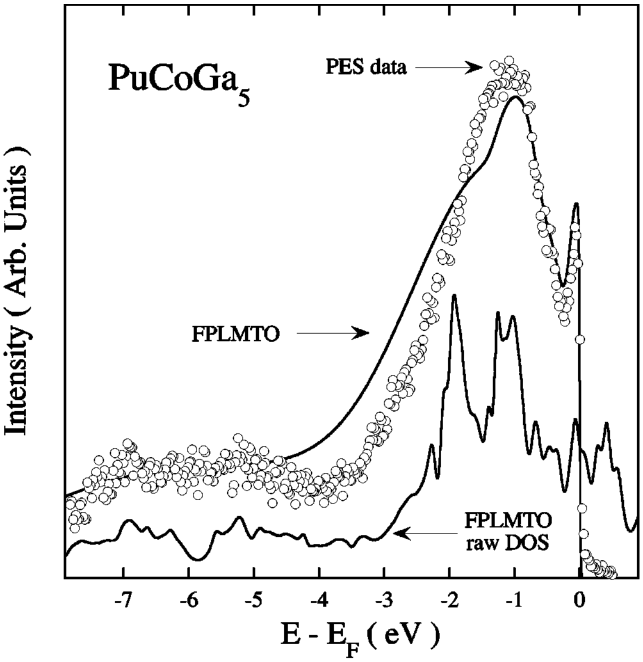

FIG. 2. PES from Joyce *et al.* (Ref. 7) together with DOS (raw DOS) and lifetime broadened DOS, obtained from an antiferromagnetic calculation.

IV. CONCLUSIONS

The nature of the 5f electrons in the $PuCoGa_5$ superconducting compound has been addressed by means of first-principles calculations. Our calculations suggest, in agreement with previous studies,[3–5] that the 5f electrons are fully itinerant with a substantial presence at the Fermi level. The question of magnetism[3] is addressed by comparing calculations with PES. These comparisons support a magnetic over a nonmagnetic theoretical treatment. The proposal[7] that the 5f manifold must be divided into localized and itinerant subsets to agree with PES is shown not to be necessary. Hence, first-principles computations, assuming delocalized 5f electrons that are allowed to correlate through spin and orbital interactions, reproduce sensitive crystallographic details and PES extremely well. This gives good credence to the theory which may prove to be helpful in understanding the superconducting mechanism in $PuCoGa_5$.

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