Superconductivity Caused by the Pairing of Plutonium $5f$ Electrons in PuCoGa$_5$

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(Received 27 September 2002; published 15 April 2003)

On the basis of electronic structure calculations we identify the superconductivity in the novel, high-temperature superconductor PuCoGa$_5$ to be caused by the pairing of Pu $5f$ electrons. Assuming delocalized Pu $5f$ states, we compute theoretical crystallographic constants very near to the experimental ones, and the calculated specific heat coefficient compares reasonably to the measured coefficient. The theoretical Fermi surface is quasi-two-dimensional and the material appears to be close to a magnetic phase instability.

A new group of fascinating heavy-fermion superconductors that crystallize in the HoCoGa$_5$ structure was discovered a few years ago [1]. Among the superconductors of this group that have drawn wide attention are CeCoIn$_5$, CeRhIn$_5$, and CeIrIn$_5$ [1–3]. CeCoIn$_5$ and CeIrIn$_5$ are superconductors at ambient pressure [2,3], with $T_c = 2.3$ and 0.4 K, respectively, whereas CeRhIn$_5$ becomes a superconductor (with $T_c = 2.1$ K) under pressure [1]. At ambient pressure CeRhIn$_5$ orders antiferromagnetically with an incommensurate spin spiral below the Néel temperature $T_N = 3.9$ K [4]. The entanglement of heavy-fermion behavior, antiferromagnetism, and superconductivity points towards an unconventional pairing mechanism. Experimental evidence for unconventional superconductivity in CeRhIn$_5$ and CeCoIn$_5$ was recently reported [5–7].

After the initial discovery of these Ce-based superconductors, investigations of other materials in this composition were undertaken. Recently, the discovery of superconductivity in PuCoGa$_5$ at an astonishing T_c as high as 18.5 K was reported [8]. A T_c of 18.5 K is an extremely high value for an actinide material and an unprecedented value for a Pu-based material. Single crystals of PuCoGa$_5$ have been synthesized which proved this material to crystallize in the HoCoGa$_5$ structure [8].

Here we report a computational investigation of the crystallographic and electronic structure of PuCoGa$_5$. From full-potential, relativistic total-energy calculations we determine the equilibrium theoretical lattice parameters of PuCoGa$_5$ in the tetragonal HoCoGa$_5$ structure (i.e., a, c/a, and the specific Ga z coordinate). For the optimized lattice parameters we investigate in detail the electronic structure of the material. This includes the total energy of the paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AFM) phases, the energy bands, partial density of states, and Fermi surface. We particularly investigate the character of the bands at the Fermi energy (E_F). In contrast to the Ce-based superconductors, where the $4f$ electrons appear to be localized [9], we establish for PuCoGa$_5$ that the energy bands at E_F consist dominantly of delocalized Pu $5f$ states. This point

is of utmost relevance for determining what kind of electrons form the Cooper pairs in the superconducting state, and what the mechanism responsible for the pair formation could be. The implications of the computed electronic structure for the unexpected superconductivity are examined.

Methodology.—We performed band-structure calculations using the fully relativistic extension [10] of the full-potential local orbitals minimum-basis band-structure method [11]. In these calculations, the following basis sets were adopted: the $5f$; $6s6p6d$; $7s7p$ states of Pu were treated as valence states, while for Co and Ga we used $3d$; $4s4p$, and $3d$; $4s4p4d$, respectively. The high-lying $6s$ and $6p$ semicore states of Pu, which might hybridize with the $6d$ and $5f$ valence states, are thus included in the basis. For the site-centered potentials and densities we used expansions in spherical harmonics up to $l_{max} = 12$. The number of k points in the irreducible part of the Brillouin zone was 196, but calculations were made also with 405 and up to 2176 k points to resolve the density of states at E_F. The Perdew-Wang [12] parametrization of the exchange-correlation potential in the local spin-density approximation (LSDA) was used.

As mentioned above, one important question concerns the degree of localization of the Pu $5f$ states. It is well known that in the actinide series around Pu a transition occurs from delocalized $5f$ states in the lighter actinides to localized $5f$'s in the heavier actinides (see, e.g., [13]). It is currently being debated whether the δ phase of elemental Pu is to be described with delocalized or localized $5f$ states [14,15]. In the case of Pu compounds, ligand-hybridization effects may modify the localization behavior of the $5f$'s. It has been found, for example, that the Pu $5f$'s are rather localized in PuSb [16], whereas for PuSe the $5f$'s appear to be relatively delocalized [17]. For PuCoGa$_5$ we adopt here, as a starting point, the assumption of delocalized $5f$ states, for which the LSDA should be appropriate. The validity of the delocalized LSDA description can be proven only from a comparison of calculated and experimental properties. Such comparison is performed here for those properties available.

Results.—The tetragonal HoCoGa$_5$ crystal structure
($P4/mmm$ space group) of PuCoGa$_5$ can be viewed as
an alternating stack of PuGa$_3$ and CoGa$_2$ units along the c
axis. It has one specific, internal Ga z coordinate [8]. We
optimized the lattice parameters a, c/a, and Ga z coor-
dinate from *ab initio* total-energy calculations for the
PM, FM, and AFM phases; see Fig. 1. We find that the
total energies of the FM and AFM phases are nearly
identical; hence it cannot exclusively be established
which phase is the theoretical ground state. Both magneti-
cally ordered phases are lower in energy than the PM
phase by 0.02 Ry. The calculated lattice constants are
$c/a = 1.602$, $z(\text{Ga}) = 0.304$, and $a = 4.15$ Å for the
magnetic phases ($a = 4.12$ Å for the PM phase). These
values are to be compared to the experimental data, $a =$
4.232 Å, $c/a = 1.603$, and $z(\text{Ga}) = 0.312$. The calculated
basal-plane lattice constant a is 1.9% smaller than the
experimental one (2.6% for the PM phase). Such deviation
is in the acceptable range of LSDA band-structure calcu-
lations. An important conclusion which follows from the
attained agreement is that the starting assumption of
delocalized 5f states is proven to be justified. This is a
decisive finding, in particular, with regard to the ongoing
debate over the description appropriate for the 5f's of
δ-Pu, localized [14] or delocalized [15]. We emphasize
that our theoretical lattice optimization was performed
before data on single crystals became available. Before
these data became at our disposal, only the lattice con-
stants of UCoGa$_5$ were known [18], which we now know
to be very close to those of the Pu-based compound. A
sizable change in the lattice constants could indicate a
transition to localized 5f's, but consequently there is no
indication of such a transition.

A systematic experimental study of the magnetic prop-
erties of PuCoGa$_5$ was not yet conducted, but so far
long-range magnetic order was not reported. The only
measured magnetic quantity is the susceptibility, which
showed Curie-Weiss behavior with an effective moment
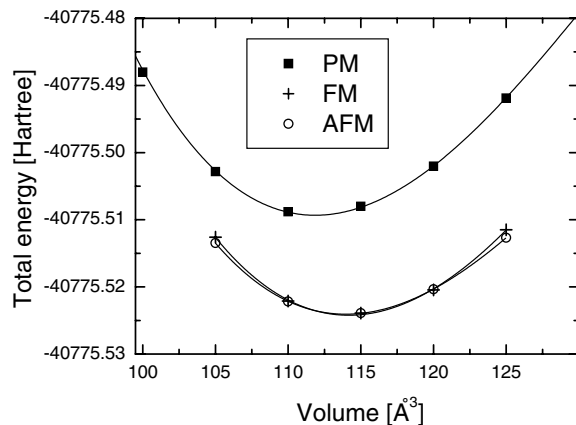close to that expected for Pu^{3+} at elevated temperatures

[8]. Since Pu^{3+} is a magnetic ion, it is evident that
magnetic interactions must be present. The clarification
of magnetic order has to await future experimental stud-
ies. In expectancy of these, we shall in the following
consider both the PM and the magnetic phases. We note
that there is a large cancellation of the site-projected Pu
spin ($4.08\mu_B$) and orbital moment ($-2.32\mu_B$) in the
magnetic phases, leading to a computed equilibrium Pu
total moment of $1.76\mu_B$ for both magnetic phases. The
near degeneracy of the FM and AFM states prompts that
the exchange coupling between adjacent Pu planes is
weak, reflecting the sizable Pu interlayer separation.

Next we consider the densities of state (DOS). The
calculated partial and total DOS's are shown in Fig. 2
for the PM and FM phases. In the PM phase, the Pu 5$f_{5/2}$
and 5$f_{7/2}$ spin-orbit split subbands give rise to the two
rather narrow peaks in the DOS (top panel). Most of the
DOS at E_F is due to Pu 5$f_{5/2}$ states, whereas the Ga and
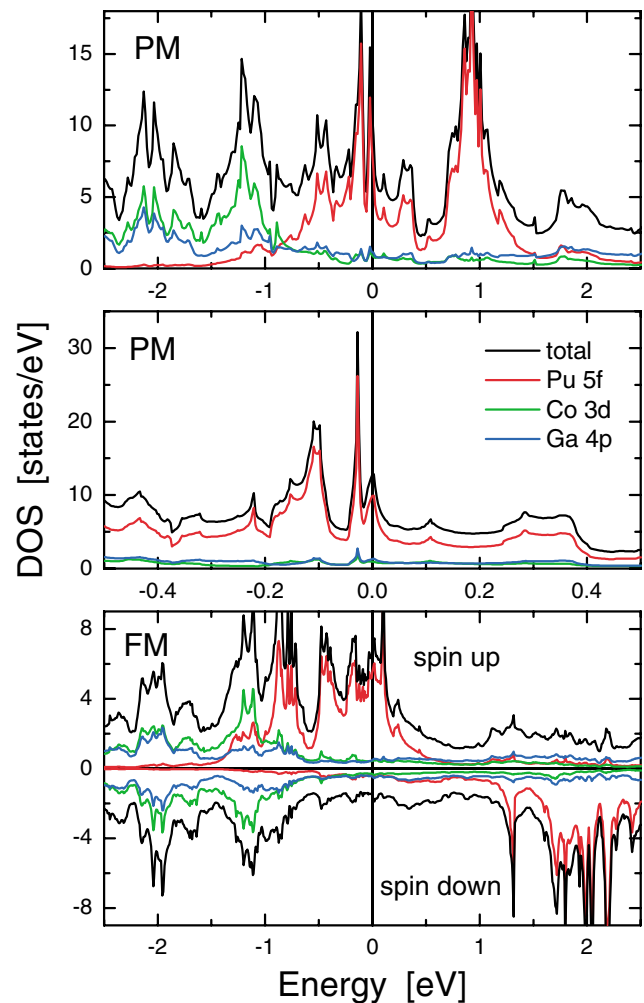Co valence states contribute much less to the DOS in the

FIG. 2 (color).   Calculated total and partial density of states
(DOS) of PuCoGa$_5$ for the optimized lattice constants. Top:
DOS of paramagnetic PuCoGa$_5$; middle: expanded view of the
PM DOS near E_F; bottom: DOS of the FM phase.

FIG. 1.   Calculated total energy vs volume for PuCoGa$_5$ in the
paramagnetic, ferromagnetic, and antiferromagnetic phases.

vicinity of E_F (middle panel). It is noteworthy that there is a huge, narrow peak in the DOS located only 20 meV below E_F which is dominated by $5f_{5/2}$ states. The proximity of this peak to E_F indicates an electronic instability of the PM state towards magnetic order. Upon magnetic ordering the narrow peak is reduced (bottom panel); however, the $5f$ states still dominate at E_F. The calculated, unenhanced specific heat coefficient is $\gamma = 23$ mJ/mol K^2 for the magnetic phases (30 mJ/mol K^2 for the PM phase). The former value is smaller by a factor 2.5 to 3.3 than the experimental specific heat coefficient, which is estimated to be $\gamma \approx 58$–77 mJ/mol K^2 above T_c [8]. A many-body enhancement of three is already for transition-metal compounds normal. In the case of actinides it suggests that the calculated energy bands in the vicinity of E_F describe the electronic structure without significantly being renormalized. The situation is markedly different for the related Ce-based heavy-fermion superconductors, for which specific heat coefficients of about 300 to 750 mJ/mol K^2 were reported [2,3], indicating substantial renormalization effects.

The character of the PM bands in an interval of -1 to 1 eV about E_F is displayed in Fig. 3. The $5f$ character of the bands is illustrated by their fatness. The bands in the vicinity of E_F consist nearly completely of the Pu $5f_{5/2}$ states. The Pu $5f_{7/2}$ states give rise to the hole pockets at Γ and X. The contributions from the d states of Co and the p states of Ga are not shown, because their contribution is much smaller than that of the Pu $5f$ states. There exists only a minor admixture of the Ga p states in the band part at the Γ point. The energy bands at E_F in the magnetic phases are dominated by the Pu $5f$ states as well, but not shown for brevity's sake.

The calculated Fermi surface of PM PuCoGa$_5$ is presented in Fig. 4. There are five Fermi surface sheets: A spherically shaped hole pocket centered at the Γ point, a hole ellipsoid at the X point, one somewhat rectangular tube along the A-M-A edge of the Brillouin zone, a further tube along the z axis, and a more open tube structure along the A-M-A edge. The colors of the Fermi surfaces indicate the relative sizes of the Fermi velocities (i.e., $\partial E/\partial k$) on the sheets. A high Fermi velocity is expressed by the red color, a small Fermi velocity by the dark blue color. The velocities on the two hole pockets are the highest, which partially is related to the higher curvature of these small surfaces. Except for these small hole pockets, the Fermi surface exhibits a pronounced two-dimensionality. Such two-dimensionality must obviously be reflected in the transport properties of PuCoGa$_5$, for which, however, no data are available as yet. A pronounced two-dimensionality was computed for the magnetic phases also. The source of the two-dimensionality is the layered crystal structure that consists of Pu-Ga layers—bearing most of the transport—separated by Co-Ga layers.

Discussion.—Our *ab initio* calculations show that the behavior of the Pu $5f$ electrons in the new Pu-based
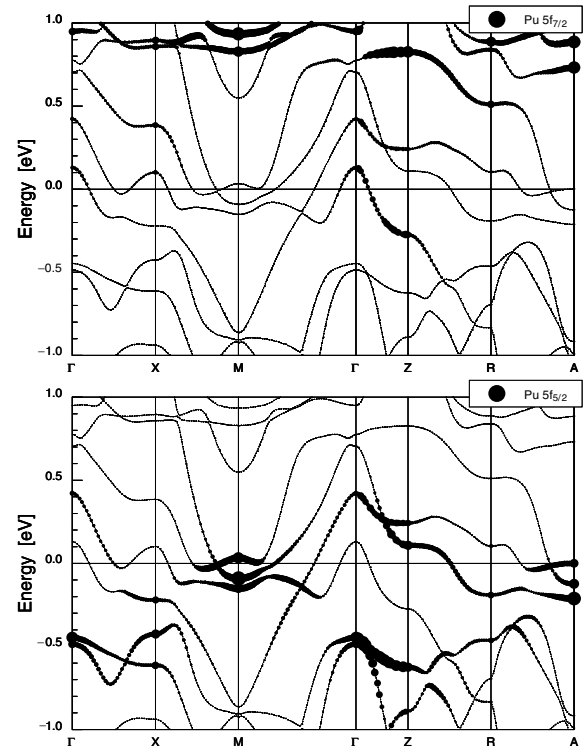
FIG. 3.   Character of the energy bands of PM PuCoGa$_5$ about the Fermi level. The thickness of the dots indicates the amount of Pu $5f_{7/2}$ states (top), $5f_{5/2}$ (bottom), respectively, present in each band.

superconductor is distinct from that of the Ce $4f$ electrons in the Ce-based superconductors. Although at first it was speculated for CeRhIn$_5$ that the Ce $4f$ electrons might be delocalized [19], a careful analysis of the de Haas–van Alphen data showed the Ce $4f$ electrons to be localized [9]. The $4f$ electrons are not placed at E_F and, hence, do not participate in the pair formation. Nonetheless, the $4f$ electrons are responsible for the magnetism which could, for example, through spin degrees of freedom, give rise to an unconventional pairing interaction. The superconductivity in the Pu-based compound arises, consequently, out of physically very different electronic states as compared to the Ce-based analogs. The fact that the T_c in the Pu compound is nearly an order of magnitude *larger* than that of the Ce-based compounds, in spite of its DOS at E_F (as inferred from the specific heat) being an order of magnitude *smaller,* exemplifies that mechanisms play a role in a distinct manner.

We discern four aspects to be important for unraveling the superconductivity, which are the two-dimensional Fermi surface, the near degeneracy of magnetic phases, the observed absence of Pauli limiting in the upper-critical field H_{c2}, and the reduction of T_c due to self-radiation damage [8]. The last observation indicates superconductivity in the clean-limit regime. The absence of Pauli limiting in H_{c2} [8] suggests particularly two possible scenarios. If the absence of Pauli limiting is confirmed at low temperatures the superconductivity
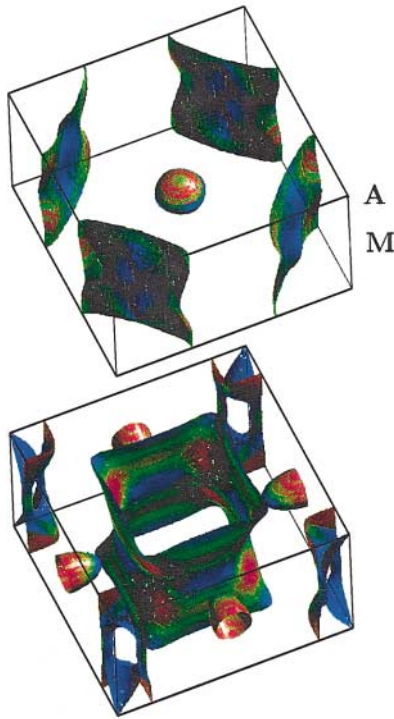
FIG. 4 (color). Calculated Fermi surface of PM PuCoGa$_5$. Apart from the two small hole pockets at the Γ point (at the center) and at the X point (middle of the facets), the Fermi surface displays a pronounced two-dimensionality. Colors indicate the size of the Fermi velocity: blue corresponds to a small velocity, and red to a large velocity.

would likely be unconventional, due to spin-triplet pairing. Conversely, if some form of Pauli limiting sets in at low temperatures (yet above the Clogston limit [20]) the superconductivity would rather be spin-singlet pairing, yet the gap may exhibit line nodes. This is the situation, e.g., for CeCoIn$_5$, where line nodes with $d_{x^2-y^2}$ symmetry were identified [21]. In either case, it appears that the superconductivity in this material cannot be captured by a simple, isotropic single band approach, but rather a multiband approach is called for. The multiband approach would heavily bear on the anisotropic, two-dimensionality of the Fermi surface. This feature of the Fermi surface will cause an anisotropic H_{c2} already for an isotropic, nodeless gap. The two-dimensionality is a reminder of similar findings reported for MgB$_2$, which has very two-dimensional Fermi sheets as well as more isotropic Fermi surface parts. Differences in the electronic coupling on the different surfaces leads to superconducting gaps of different sizes being present on each type of surface [22]. If a similar situation would occur for the Pu compound the intriguing question is obviously what pairing mechanism causes the different coupling on different sheets. A suggestion for a unique pairing mechanism stemming from 5f electrons being on the border between localized and itinerant has already been proposed [8]. Our present investigation emphasizes the occurrence of magnetic interactions between the 5f electrons. The proximity of FM and AFM states signals, in particular, a weak interlayer exchange coupling that could concurrently give rise to soft spin fluctuations. Adding to this, the unusually high T_c and the mentioned absence of Pauli limiting, it appears reasonable to speculate that a magnetic interaction between the 5f electrons plays a role in the pairing. In this aspect PuCoGa$_5$ is similar to its Ce-based analogs [21], yet the hybridization of the 5f's is much stronger, leading to a stronger coupling, and thus to a higher T_c.

To conclude, our calculations identify the superconductivity in PuCoGa$_5$ to emerge out of electronic states dominated by Pu 5f electrons. A critical test of the calculated electronic structure in the vicinity of E_F would be de Haas–van Alphen measurements and photoemission experiments. The latter could provide decisive information about the binding energy of the 5f electrons.

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