Magnetism, Spin-Orbit Coupling, and Superconducting Pairing in UGe_2

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A consistent picture on the mean-field level of the magnetic properties and electronic structure of the superconducting itinerant ferromagnet UGe_2 requires inclusion of correlation effects beyond the local density approximation (LDA). The "LDA + U" approach reproduces both the magnitude of the observed moment and the magnetocrystalline anisotropy. The largest Fermi surface sheet is composed primarily of spin majority states with orbital projection $m_\ell = 0$, suggesting a much simpler picture of the pairing than is possible for general strong spin-orbit coupled materials. The quasi-two-dimensional geometry of the Fermi surface supports the likelihood of magnetically mediated p-wave triplet pairing.

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The coexistence of superconductivity with magnetism has recently reemerged as a central topic in condensed matter physics, due to competition between ordering of magnetic ions and superconducting pairing in borocarbides [1], to unprecedented coexistence of magnetic order with substantial ferromagnetic component with high-temperature conductivity [2–4] and to observation of magnetic → superconducting transitions near quantum critical points in f electron systems such as $CeRh_2Si_2$ [5], $CeIn_3$ [6], $CePd_2(Si, Ge)_2$ [7], and $CeRhIn_5$ [8]. Superconductivity below 1 K in the limited pressure range (1 to 1.6 GPa) was recently observed coexisting with strong ferromagnetism in a high purity single crystal UGe_2 [9,10] adding yet another dimension to this unanticipated phenomenon of phase coexistence. This superconducting phase is found *within* the ferromagnetic phase and disappears in the paramagnetic region, strongly suggesting the pairing mechanism is magnetic in origin.

There are no other known examples of superconductivity coexisting with *strong* ferromagnetism (average moment comparable to Ni, say). This phenomenon necessarily requires triplet spin pairing (or more precisely, an odd symmetry real space pair) since the exchange split bands (and the very different Fermi surfaces) preclude singlet pairing. The normal state symmetry itself is low in spite of the relatively simple crystal structure of UGe_2. Magnetism breaks time reversal invariance, leaving the normal state symmetry consisting of the product of the magnetic space group and gauge invariance [$\mathcal{G} \times$ U(1)], the latter of which is always broken by the onset of superconductivity. The possible order parameter symmetries are very limited.

Recent experiments on single crystals [11,12] indicate UGe_2 (previously thought to crystallize in the *Cmcm* $ZrSi_2$-type structure) actually has the base-centered orthorhombic $ZrGa_2$ crystal structure (*Cmmm*). The structure, shown in Fig. 1, can be viewed as consisting of antiphase zigzag chains of U atoms running along the $\hat{a}$ direction and lying within the $\hat{a} - \hat{b}$ plane; however, interchain and intrachain separations are comparable. Each U is tenfold coordinated by Ge. Importantly, the structure possesses inversion symmetry. Single crystal magnetization measurements [13] and neutron powder diffraction measurements [12] both yield a collinear magnetic structure with the ferromagnetically ordered magnetic moment of $1.42\mu_B$. (We quote moments per formula unit, i.e., per U atom.) The Curie temperature $T_c = 52$ K at ambient pressure decreases under pressure, vanishing at 1.6 GPa. Around 1 GPa, Saxena *et al.* [10] have found that UGe_2 becomes superconducting while remaining strongly ferromagnetic ($\overline{M} \approx 1\mu_B$/U) providing a novel example of coexistence of the superconductivity with strong ferromagnetism.

Magnetic measurements [13,14] yield very strong magnetocrystalline anisotropy in UGe_2 with easy magnetization axis along $\hat{a}$ (the shortest crystallographic axis, Fig. 1). It was found [13] that even in high magnetic field (up to 35 T) it is impossible to saturate magnetization

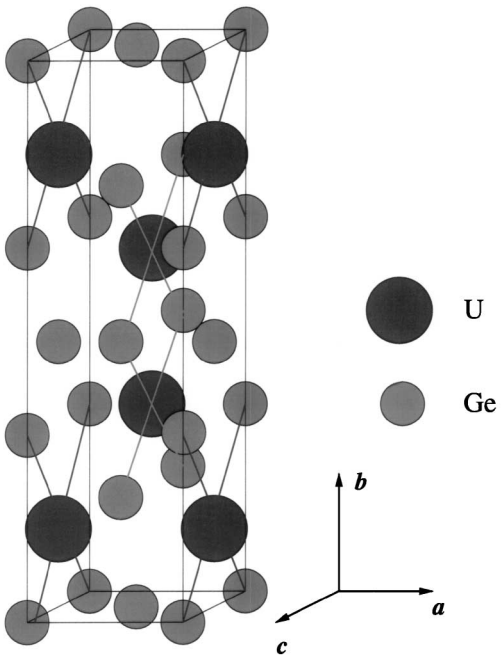

FIG. 1. The base-centered orthorhombic *Cmmm* crystal structure of UGe_2. The volume shown includes two primitive cells.

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along the hard $\hat{b}$ and $\hat{c}$ axes. Such highly anisotropic behavior is typical of magnetic $5f$ electron materials. Susceptibility measurements [10] above T_C yield an effective paramagnetic moment $m_{\text{eff}} \approx 2.7\mu_B$/U which differs from the atomic value of $3.62\mu_B$ for atomic f^3 configuration, indicating substantial $5f$ hybridization with conduction states. Moreover, the carriers with the high cyclotron masses of $(15 - 25)m_0$ were observed in dHvA experiments [15] suggesting itinerant but strongly correlated $5f$-electron states. UGe_2 is, however, not a real heavy-fermion system since its electronic specific heat coefficient $C(T)/T = \gamma \approx 35$ mJ/K^2 mol is about 10 times smaller than in conventional heavy-fermion U compounds [14].

The electronic and magnetic structure of UGe_2 is a rather open issue. Yamagami *et al.* [16] reported the results of relativistic augmented-plane-wave calculations, but without interplay between magnetism and spin-orbit coupling (SOC) and using the old crystal structure. The scope of this paper is to provide a microscopic picture of electronic structure and magnetism of ferromagnetic UGe_2 upon which models of the superconductivity can be based. This picture leads to specific indications of the pairing character in UGe_2.

We first applied conventional band theoretical methods in the local density approximation using a relativistic full-potential linearized augmented plane wave method [17]. The results did not reproduce the observed ground state moment [12,13]. The calculated spin magnetic moment ($M_s = 1.57\mu_B$) is canceled by the orbital moment arising from spin-orbit coupling ($M_L = -1.84\mu_B$ [18]) yielding the net moment of $|M| = 0.27\mu_B$, 5 times smaller than the experimental value of $1.4\mu_B$. The cause is due to the oversimplified treatment of correlation effects, as is often seen in the application of local density approximation (LDA) to f electron materials.

We therefore account for the on-site atomiclike correlation effects beyond LDA by using the LDA + U approach [19] in a rotationally invariant, full potential implementation. Minimizing the LDA + U total energy functional with SOC treated self-consistently [17] generates not only the ground state energy and spin densities, but also effective one-electron states and energies (the band structure) that provides the orbital contribution to the moment and Fermi surfaces. The basic difference of LDA + U calculations from the LDA is its explicit dependence on the on-site spin and orbitally resolved occupation matrices [20]. Since the LDA + U method is rarely applied to metals, the appropriate values of the on-site f electron repulsion U and exchange J constants are not known. Our values of $U = 0.7$ eV, $J = 0.44$ eV were chosen to reproduce the ground state magnetic moment $M_J = M_s + M_l$. Mainly U was varied, but it seemed to be of some importance to reduce J slightly from its atomic value of 0.55 eV [21] to keep U from becoming unreasonably small. The resulting total uranium f-electron occupation ($2.8e$) is close to but clearly less than the f^3 configuration. The value of Coulomb U differs from the "atomiclike" value of $U = 2$ eV which was derived for U f^3 compounds in Ref. [21]. The reduction of the Coulomb U to 0.7 eV in order to obtain the correct value for the magnetic moment reflects the partly itinerant character of the U $5f$ states and accounts for the metallic screening of the U $5f$ states in UGe_2.

To probe the magnetic ground state we calculated the energy of one antiferromagnetic configuration in addition to ferromagnetic, where the two U atoms in the unit cell (in the "chain" in Fig. 1) had antialigned moments. Nearest neighbors between chains there were also antiparallel. The ferromagnetic alignment is 32 meV/f.u. lower in energy, consistent with the observed ferromagnetism.

To study the magnetic anisotropy we performed the total energy calculations for the magnetic moment along each of the $\hat{a}$, $\hat{b}$, and $\hat{c}$ axes. The orthorhombic crystal symmetry was reduced in order to preserve the projection of the orbital moment along the spin direction. To obtain convergence for the total energy differences we used 275 k-points in 1/4 of the Brillouin zone (BZ) for the magnetization along $\hat{a}$ and $\hat{b}$, and 250 k-points for $\hat{c}$ orientation; these meshes are equivalent to 1000 k-points in the BZ. The total energy differences yield the magnetic anisotropy energy and are shown in Table I. The calculations produce easy magnetization axis $\hat{a}$ in accord with the experiment. There is a pronounced anisotropy for both spin M_s and orbital M_L magnetization reflecting the interplay between the strong spin-orbit coupling (the SOC constant $\xi = 0.22$ eV) and the large exchange splitting. The variation of the spin and orbital moments with orientation is 7%–10% (Table I), and manifests itself in strong, qualitative differences in the band structure and Fermi surfaces. Thus it is *crucial* to use the easy axis orientation, and henceforward we discuss only this case.

This strong magnetic anisotropy (2–3 orders of magnitude larger than in $3d$ ferromagnets) reflects the strong spin-orbit coupling for $5f$ states and is consistent with the reported experimental data for the magnetocrystalline anisotropy energy (MAE) in the uranium compounds [22]. It explains qualitatively the difference in the measured magnetization values for single crystals ($1.42\mu_B$) and polycrystals ($1.07\mu_B$ [12], $0.5\mu_B$ [14]): since the magnetic moment is kept by magnetic anisotropy along

TABLE I. The U $5f$ state occupation (n_f), spin (M_S), orbital (M_L), and absolute value of net ($|M_J|$) magnetic moments (μ_B) for three directions of magnetization. The magnetocrystalline anisotropy energy (MAE in mRy/f.u.) is the total energy difference MAE $\equiv E_{b(c)} - E_a$ for the magnetization as indicated.

	n_f	M_S	M_L	$\lvert M_J\rvert$	MAE
$\hat{a}$	2.81	1.52	−2.98	1.46	0
$\hat{c}$	2.80	1.41	−2.85	1.43	0.67
$\hat{b}$	2.81	1.62	−3.18	1.56	0.55
Expt. [12,13]				1.42	

the easy magnetization direction ($\hat{a}$) in each grain of the polycrystal, the average measured moment should be reduced but should exceed 1/3 of its single crystal value.

The complex band structure contains 7 orbitals $\times$ 2 U atoms $\times$ 2 spins = 28 primarily U $5f$ bands within a 3 eV region spanning the Fermi energy E_F. They are of mixed spin character due to SOC and contain only minor Ge $4p$ character, which is mostly below and above the U $5f$ bands. Bands crossing the Fermi level have predominantly U $5f$ character and mostly spin majority character. These bands have low dispersion along k_y ($\hat{b}$ direction) indicating an $\hat{a}$-$\hat{c}$ plane quasi-two-dimensional (quasi-2D) character of the UGe_2 electronic structure near E_F. The exchange splitting, to the extent that an average can be defined when there is strong SOC, is about 20 times as large (1–1.5 eV) as suggested by Yamagami *et al.* [16] based on unpolarized calculations.

Since the LDA + U potential is formulated in terms of m_s and m_l rather than the total moment m_j, it is natural to perform a spin and orbital resolution $\{m_s; m_l\}$. The combination of strong spin polarization and large SOC results in a remarkably clean $\{m_s; m_l\}$ separation as is evident in Fig. 2. The peak in the vicinity of E_F is formed by $\{\uparrow; 0\}$ and $\{\downarrow; 1\}$ states coupled by spin orbit; $N(E_F)$/f.u. = 1.7 and 0.7 states/eV, respectively. The total $N(E_F)$/f.u. of 5.5 states/eV is mainly (75%–80%) due to U $5f$ contributions. The measured electronic specific heat coefficient $\gamma = 35\text{mJ/K}^2$ mol [14] corresponds to a dressed value $N^*(E_F) = 15$ states/eV, indicating a dynamic enhancement $N^*(E_F)/N(E_F) = 2.7$ arising from magnetic fluctuations with possible contributions from phonons and charge fluctuations.

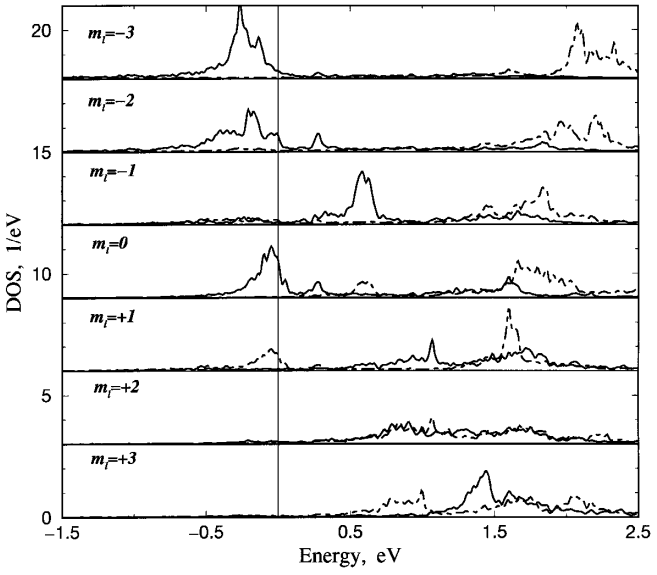

FIG. 2. Spin and orbitally resolved U $5f$ state density of states for easy axis $\hat{a}$ orientation: spin-↑ is shown in solid line; spin-↓ is shown in dashed line. Other orientations of the moment give distinctly different results.

Photoelectron x-ray photoemission spectroscopy (XPS)-Bremsstrahlung Isohromat spectroscopy (BIS) studies of UGe_2 [23] reported a pronounced broad peak in XPS spectrum $\approx$1 eV below the Fermi level. Our calculated U $5f$ density of states (fDOS) (Fig. 2) has a double peak due to $\{\uparrow; m_l = -3, -2\}$ located 0.3–0.4 eV below the Fermi level. This difference may be due to neglect of dynamical effects in our calculations but may also reflect surface state contributions in the data. In the measured BIS spectrum, which is less surface sensitive, there is a kink around 0.5 eV and a main peak at 1.3 eV above E_F. The LDA + U calculations reproduce both features: the structure at 0.5 eV arises from $\{\uparrow; -1\}$ character and the much bigger peak at around 1.5 eV is due to $\{\uparrow; +3\}$ and $\{\downarrow; 0, 1\}$ states.

The calculated Fermi surface is complex and consists of three sheets. The largest and most interesting sheet is shown in Fig. 3. The quasi-2D surface has weak dispersion along k_y, i.e., hopping between chains is small for this band. In spite of (but actually because of) the strong SOC, this surface has simple character: predominantly $\{\uparrow; 0\}$ with some mixture of $\{\downarrow; 1\}$. If, in a first approximation, this small opposite spin character can be neglected, one can consider pure spin $\{\uparrow; 0\}$ states and hence simpler models for pairing. In this limit the problem reduces to the one of so-called "single spin pairing" [24], which, however, has not been studied specifically for the low orthorhombic symmetry of UGe_2.

It was suggested some time ago [25] that superconducting p-wave (triplet) pairing for equal spin states can appear due to the longitudinal magnetic fluctuations. The roughly nesting portions of quasi-2D surfaces should promote strong magnetic interactions between spin-majority carriers located periodically in the space along magnetization direction $\hat{a}$. The rapid collapse of the moment between 1 and 1.6 GPa [10] is also consistent with

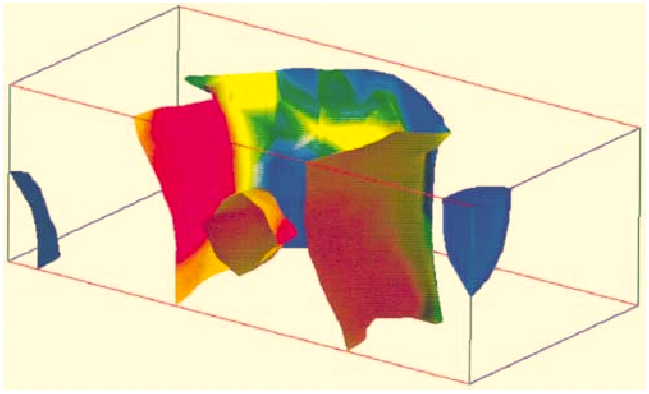

FIG. 3 (color). The Fermi surface for UGe_2 that is discussed in the text. The zone center is at the far corner of the plotted regions, and the distances plotted correspond to $\frac{2\pi}{a}, \frac{2\pi}{b}, \frac{\pi}{c}$ with axes directed as in Fig. 1. The large surface is primarily $\{m_s = \uparrow; m_l = 0\}$ character, is quasi-two-dimensional, and shows indication of a nesting feature around $(0.45\frac{2\pi}{a}, 0, 0)$.

longitudinal magnetic fluctuations. The distinctive electronic structure that we find suggests that a nonrelativistic model can be used to describe the magnetically mediated superconductivity in UGe_2.

It must be recognized that the results presented here apply only to the zero pressure and temperature. At the peak of the superconducting phase ($\sim$1 GPa) the moment is reduced by 1/3 and the lattice constants and internal coordinates will be changed. Consequently, the exchange splitting will decrease and bandwidths will be increased, altering the Fermi surface from the one we have presented. The general features of the $(m_s; m_\ell)$ fDOS separation in Fig. 2 are expected to be robust.

To summarize, accounting for some correlated behavior (beyond what is included in LDA) using the LDA + U approach in a very general implementation including SOC, we have provided a microscopic picture of the electronic and magnetic character of UGe_2 that is essential for beginning to understand the coexistence of superconductivity with strong ferromagnetism. Our results are in accord with several important experimental observations (magnitude and direction of the moment, BIS spectra), and suggest a relatively simple picture of the U $5f$ bands arises in spite of the 28 f-bands that span E_F. The calculated Fermi surface has a quasi-2D sheet of predominantly majority spin character, supporting conjectures of magnetically mediated triplet superconductivity in UGe_2. The coexistence of superconductivity with magnetic order is quite distinct from that in $RuSr_2GdCu_2O_8$, with its separate magnetic superconducting layers, because in UGe_2 the magnetism and superconductivity clearly seem to be due to the same U $5f$ electrons.

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