

Electronic and magnetic structure of URhGe

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A consistent picture of the magnetic properties and electronic structure of the superconducting itinerant ferromagnet URhGe is obtained with the local spin-density approximation (LSDA). The LSDA calculations reproduce both the magnitude of the observed moment, composed of strongly opposing spin and orbital parts, and the magnetocrystalline anisotropy. It is shown that the canted magnetic structure of URhGe can originate from the noncollinear arrangement of U-atom orbital magnetic moments, while the spin magnetic moments are ferromagnetically ordered.

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Superconductivity coexisting with ferromagnetic order was recently observed in UGe₂ (Ref. 1) and URhGe.² This superconducting phase is found within the ferromagnetic phase and disappears in the paramagnetic region, strongly suggesting that the pairing mechanism is magnetic in origin. While for UGe₂ the superconductivity occurs at high pressure, URhGe is superconducting at ambient pressure. Recent theoretical studies of the electronic and magnetic structure, and superconducting pairing in UGe₂ (Refs. 3 and 4) strongly suggest *p*-wave (triplet) pairing for equal spin states due to the longitudinal magnetic fluctuations.⁵ The aim of this paper is to show that first-principles calculations account correctly for the electronic and magnetic structure of URhGe. We show that the magnetic canting in URhGe can originate from antiferromagnetic order of U-atom orbital magnetization components. The calculated electronic and magnetic properties determine the possible superconducting pairing, and they are crucial in the theoretical understanding of superconductivity in URhGe.

Recent experiments on poly-^{6,7} and single crystals⁸ indicate that URhGe has the orthorhombic TiNiSi crystal structure (*Pnma*). This structure can be viewed as arising from “zigzag” chains of U atoms along the *a* axis which are shown in Fig. 1. The U atoms in the unit cell form two “pairs” (1,2) and (3,4) [the atoms of the pair (1,2) will henceforth be referred to as U-I, and (3,4) as U-II]. The U atoms within the pairs are connected by an inversion *I* (1 → 2, 3 → 4), a 180° rotation *C*_{2y} (1 → 2, 3 → 4), and a mirror *σ*_y (1 → 1-4), both pairs accompanied by nonprimitive translations.⁹ Other symmetry operations, 180° rotations *C*_{2x} (1 → 4, 2 → 3) and *C*_{2z} (1 → 3, 2 → 4), and mirrors *σ*_x (1 → 3, 2 → 4), *σ*_z (1 → 4, 2 → 3), map the atoms U-I of pair (1,2) to the atoms U-II of pair (3,4).

The experimental magnetic studies² show that URhGe is ferromagnetic below a Curie temperature of 9.5 K and it has a low-temperature ordered moment of 0.42 μ_B per f. u., oriented along the *c* axis (*z* axis, see Fig. 1). The magnetic symmetry operations which conserve the *z* component *M*_{*z*} of the total (spin+orbital) magnetization are

$$E, I: \quad \text{U-I}(M_x, M_y, M_z) \rightarrow \text{U-I}(M_x, M_y, M_z),$$

$$\text{U-II}(M_x, M_y, M_z) \rightarrow \text{U-II}(M_x, M_y, M_z),$$

$$C_{2y}R, \sigma_y R: \quad \text{U-I}(M_x, M_y, M_z) \rightarrow \text{U-I}(M_x, -M_y, M_z),$$

$$\text{U-II}(M_x, M_y, M_z) \rightarrow \text{U-II}(M_x, -M_y, M_z).$$

Since, the U atoms within the pairs (1,2) and (3,4) should have the same magnetization, the above conditions freeze *M*_{*y*} = 0, and allow the *M*_{*x*} ≠ 0 component.

The magnetic symmetry operations which map the U atoms of pair (1,2) to pair (3,4) are

$$C_{2x}R, \sigma_x R: \quad \text{U-I}(M_x, M_y, M_z) \rightarrow \text{U-II}(-M_x, M_y, M_z),$$

$$C_{2z}, \sigma_z: \quad \text{U-I}(M_x, M_y, M_z) \rightarrow \text{U-II}(-M_x, -M_y, M_z).$$

Mapping is only possible when *M*_{*y*} = 0, and the magnetization of pair (1,2) is transformed to the magnetization of pair (3,4) as (*M*_{*x*}, 0, *M*_{*z*}) → (-*M*_{*x*}, 0, *M*_{*z*}). Thus, together with the ferromagnetic (FM) *M*_{*z*} components along the *c* axis, antiferromagnetic (AFM) *M*_{*x*} components of U pairs (1,2) and (3,4) along the *a* axis can produce noncollinear magnetic order in the *a-c* plane, without a further decrease of the magnetic symmetry.^{7,10}

The same analysis for the case when *M*_{*x*} is conserved (*a* axis) shows that *M*_{*y*} = 0 and *M*_{*z*} ≠ 0 components of different

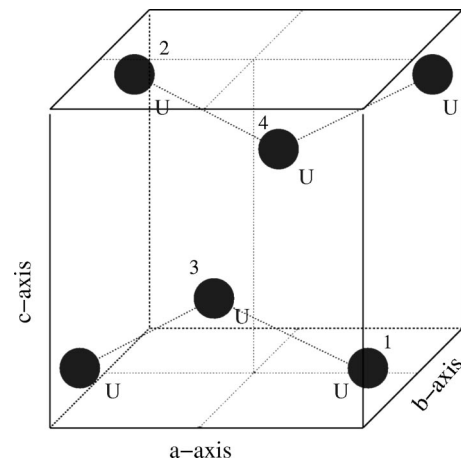


FIG. 1. Schematic crystal structure of URhGe (only U atoms are shown). The unit-cell atoms are marked as (1,2,3,4) and located at 4c sites. The crystal axes (*a*, *b*, *c*) correspond to (*x*, *y*, *z*) axes.

TABLE I. Magnetic anisotropy energy (meV/f.u.) calculated from total-energy differences for the magnetization directed along [100] (a axis), [010] (b axis), and [001] (z axis).

ΔE	[100] - [001]	[010] - [001]	[100] - [010]
Present	6.165	1.524	4.641
Reference 10	6.86	2.56	4.30

signs for the U-I and U-II atoms are allowed. For the case when M_y is conserved (b axis), both components $M_x, M_z = 0$.

The conventional local spin-density approximation (LSDA) band theoretical method is applied together with the relativistic full-potential linearized-augmented-plane-wave (LAPW) method¹¹ to perform total-energy electronic and magnetic structure calculations. First, the spin magnetization is fixed along each of the a , b , and c axes. The crystal symmetry is reduced in the presence of spin-orbit coupling in order to preserve a chosen component of the magnetization. In order to avoid systematic numerical errors when the difference in the total energies for different magnetization directions is calculated,¹² the same reduced symmetry {E,I} for all three cases¹³ is chosen. Importantly, these reduced symmetry calculations allow for two pairs of U-I atoms (1,2) and U-II atoms (3,4) to become nonequivalent with respect to conventional space-group symmetry.

Here, 144 special k points in the irreducible 1/2 part of the Brillouin Zone were used, with Gaussian smearing for k -point weighting. The ‘‘muffin-tin’’ radius values of $R_{MT} = 2.9$ a.u. for U, $R_{MT} = 2.35$ a.u. for Rh, $R_{MT} = 2.3$ a.u. for Ge, and $R_{MT}^{Ge} \times K_{max} = 7.6$ (where K_{max} is the cutoff for the LAPW basis set) were used.

The magnetic anisotropy energy (MAE) is calculated as the difference in the total energies for different orientations of the magnetic moment along the a , b , and c axes, and is shown in Table I. Total-energy calculations yield the c axis to

be the easy magnetization axis and the a axis the hard magnetization axis, in good quantitative agreement with recent experimental^{2,7,8} and theoretical¹⁰ studies. Note that the MAE of 6.165 meV/f.u. in the a - c plane is substantially higher than the MAE of 1.524 meV/f.u. in the b - c plane meaning that URhGe is the b - c easy magnetization plane ferromagnet.

The spin, orbital, and total magnetic moments for U atoms together with the total magnetic moment (per f.u.) are shown in Table II for three fixed directions of spin magnetization. For the physical case with the spin moment M_s aligned along the easy c axis, there is a total magnetic moment of $0.293\mu_B$ along the c axis arising from noncompensated U-atom spin and orbital magnetizations. The value of the total magnetic moment agrees perfectly with the previous theoretical result of $0.3\mu_B$.¹⁰ Both present calculations and those of Ref. 10 yield the total magnetic moment, which exceeds the experimental value of $0.214\mu_B$ (Ref. 8) for the single crystals, and is slightly smaller than the magnetic-moment value of 0.42 – $0.43\mu_B$ found for polycrystalline URhGe samples. Since the U-I has $(M_I^x, 0, M_I^z)$ components of the orbital magnetization and U-II has $(-M_I^x, 0, M_I^z)$ components, they contribute to the FM component along the c axis and the AFM component along the a axis yielding the magnetic canting in the a - c plane along the c axis which is experimentally observed in Refs. 2 and 7.

For M_s aligned parallel to the a axis, there is almost complete compensation of spin and orbital magnetic moments along the a axis, resulting in an almost zero total magnetic moment. This is in quantitative agreement with the magnetization measurements of Ref. 8, which report almost zero spontaneous magnetization when aligned along the a axis. Since the U-I has $(M_I^x, 0, M_I^z)$ components of the orbital moment and U-II has $(M_I^x, 0, -M_I^z)$ components, they contribute to the FM component along the a axis and the AFM component along the c axis yielding magnetic canting in the a - c plane along the a axis. When $M_s \parallel b$ axis, the U-I and U-II atoms both have $(0, M_I^y, 0)$ components of the orbital magne-

TABLE II. Spin (M_s), orbital (M_l), and total ($M_J = M_s + M_l$) magnetic moments for U atoms, and the total magnetic moment (M^{Tot}) per formula unit (μ_B) calculated for three fixed directions of spin magnetization: x (a axis), y (b axis), and z (c axis).

$M_s \parallel a$ axis [100]									
Atom	M_s			M_l			M_J		
axis	x (a)	y (b)	z (c)	x (a)	y (b)	z (c)	x (a)	y (b)	z (c)
U-I	.995	0	0	-1.005	0	-.038	-.010	0	-.038
U-II	.995	0	0	-1.005	0	.038	-.010	0	.038
M^{Tot}	.965	0	0	-1.017	0	0	-.052	0	0
$M_s \parallel b$ axis [010]									
U-I	0	1.003	0	0	-1.210	0	0	-.207	0
U-II	0	1.003	0	0	-1.210	0	0	-.207	0
M^{Tot}	0	.975	0	0	-1.224	0	0	-.249	0
$M_s \parallel c$ axis [001]									
U-I	0	0	1.033	-.027	0	-1.294	-.027	0	-.261
U-II	0	0	1.033	.027	0	-1.294	.027	0	-.261
M^{Tot}	0	0	1.011	0	0	-1.304	0	0	-.293

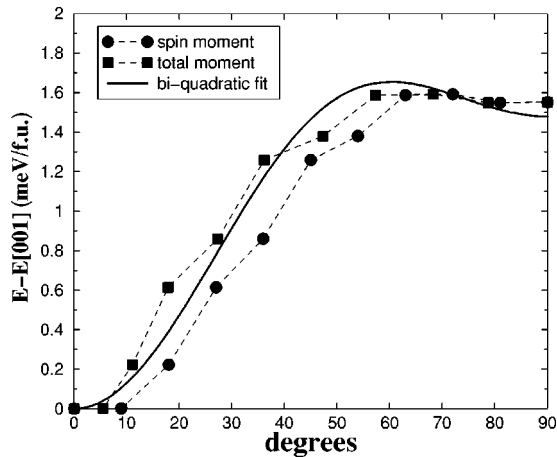


FIG. 2. Total energy vs angle θ between the c axis and the spin (circles) and total (squares) magnetization in the b - c plane, and biquadratic fit $E_{anis} = K_2 \sin^2 \theta + K_4 \sin^4 \theta$.

tization, and the magnetic order is collinear along the b axis for both spin and orbital magnetic moments. The calculated total magnetic moment of $0.249 \mu_B$ is somewhat smaller than the experimental value for single-crystal spontaneous magnetization of $0.346 \mu_B$.⁸

Note that all three calculated magnetic structures are consistent with the magnetic symmetry considerations above. It is fairly unusual that in spite of FM ordering of the spin magnetic moments there is AFM ordering of the orbital magnetic moments. This is not forbidden by the magnetic symmetry considerations and it indicates different coupling of spin and orbital magnetization to the crystal lattice.

The AFM canting of U-atom magnetic moments was proposed in Ref. 7 on the basis of neutron powder-diffraction experiments. The authors reported the U-I and U-II atoms' magnetic moments which are canted in the a - c plane with an angle of $\approx \pm 30^\circ$ off the c axis, with the absolute value of $0.26 \mu_B$ for the AFM component of the magnetization. More recent results for polycrystals² do not reproduce the picture of Ref. 7. They give the AFM component in a - c plane which has a magnitude smaller than $0.06 \mu_B$, while the FM-ordered component of $0.37 \mu_B$ is aligned along the c axis. The results of Ref. 2 are in good quantitative agreement with present calculations (see, Table II) yielding the AFM component of $0.03 \mu_B$ and FM component of $0.293 \mu_B$. Therefore, we suggest that the canted magnetic structure of URhGe can originate from the noncollinear arrangement of the orbital magnetic moments on (1,2) and (3,4) U-atom pairs (see, Fig. 1). It should be noted that the results presented here do not exclude the possibility of a noncollinear spin arrangement.

Very recent single-crystal experiments⁸ report no AFM component in the a - c plane. Instead, they suggest the magnetization to be collinear and confined to the b - c plane away from the high-symmetry axes. We perform the total-energy calculations rotating the magnetization in the b - c plane.¹⁴ The change in the total energy with the angle between magnetic moments and the c axis is shown in Fig. 2 for both spin and total magnetizations. Here, the spin magnetic moment M_s and orbital moment M_l are antialigned and not parallel to each other. Since the absolute value of M_l exceeds M_s , the

resulting total magnetic moment $\vec{M}_J = \vec{M}_s + \vec{M}_l$ in the b - c plane forms the $180^\circ + \theta_{tot}$ angle with the c axis, when the spin magnetic moment is aligned at a θ_s angle. The angle $\theta_{tot} - \theta_s$ between M_J and M_s decreases as the moments approach the a or b axes, with a maximum around 45° .

The total energy as a function of angle is very flat near both the c easy axis and b axis, indicating the possibility of additional minima close to the c and b axes. The accuracy better than 0.02 meV for the difference in the total energies of $\approx 4 \times 10^6$ eV would be required to resolve possible minima, which are practically unreachable.¹⁵ No additional minima in the b - c plane are found, contrary to the proposal of Ref. 8. Instead, there is a maximum in the total energy at $\approx 60^\circ$. It can be understood to originate from the competing second- (K_2) and fourth- (K_4) order magnetic anisotropy constants. These constants can be obtained by fitting the angular dependence of the total energy by the biquadratic function $E_{anis} = K_2 \sin^2 \theta + K_4 \sin^4 \theta$. This estimate yields for K_2 the value of 4.4 meV and -2.9 meV for K_4 . Surprisingly, the absolute value of the fourth-order anisotropy is more than half the second-order anisotropy. This fairly large absolute value of K_4 could be the reason for the strong reduction of the MAE in the b - c plane (see, Table I).

The band structure of URhGe has a mixed spin character due to the spin-orbit coupling (SOC) and we discuss only the case with the moment along the easy c axis. The total density of states (DOS) and spin-resolved densities of U- f (f DOS) states are shown in Fig. 3(a). The lower-energy region from 10.5 to 8.5 eV below the Fermi level (E_F) is formed by Ge- $4s$ states. This region is separated by an energy gap of ≈ 3 eV from the main valence band. In the region from 5.5 to 3 eV below E_F there are mainly Rh- $4d$ states hybridized with Ge- $4p$ states and U- $6d$ states. Starting from 1.5 eV below E_F there are mainly U- $5f$ states [see, Fig. 3(a)]. These states are spin split by ≈ 0.5 eV and strongly dispersive in the region of 1.5 eV below to 2.5 eV above E_F . The tail of Rh- $4d$ states is extended up to 2.5 eV above E_F indicating the hybridization of Rh- $4d$ and U- $5f$ states. The spin splitting of U- $5f$ states can be interpreted in terms of Stoner-like band magnetism¹⁰ and the total-energy difference between ferro- and nonmagnetic solutions $E_{FM} - E_{NM} = -31.8$ meV/f.u. is calculated in agreement with Ref. 10, showing that the FM solution is energetically preferred.

The spin- and orbitally resolved ($\{m_s; m_l\}$) U-atom f DOS is shown in Fig. 3(b). The combination of substantial spin polarization and strong SOC (the SOC constant $\xi = 0.22$ eV) results in $\{m_s; m_l\}$ separation as is evident in Fig. 3(b). The URhGe f DOS spin and orbital character in the vicinity of E_F differs from UGe₂ (cf. Fig. 2 of Ref. 3) and the states for both $\{\uparrow; \downarrow\}$ spins are present. The total $N(E_F)/\text{f.u.}$ of 17.5 states/eV arises mainly due to the U- $5f$ contribution. The measured electronic specific-heat coefficient $\gamma = 160$ mJ/K² mol (Ref. 16) corresponds to a dressed value $N^*(E_F) = 68.6$ states/eV, indicating a dynamic enhancement $N^*(E_F)/N(E_F) = 3.91$ that arises from magnetic fluctuations with possible contributions from phonons and charge fluctuations. The presence of magnetic fluctuations

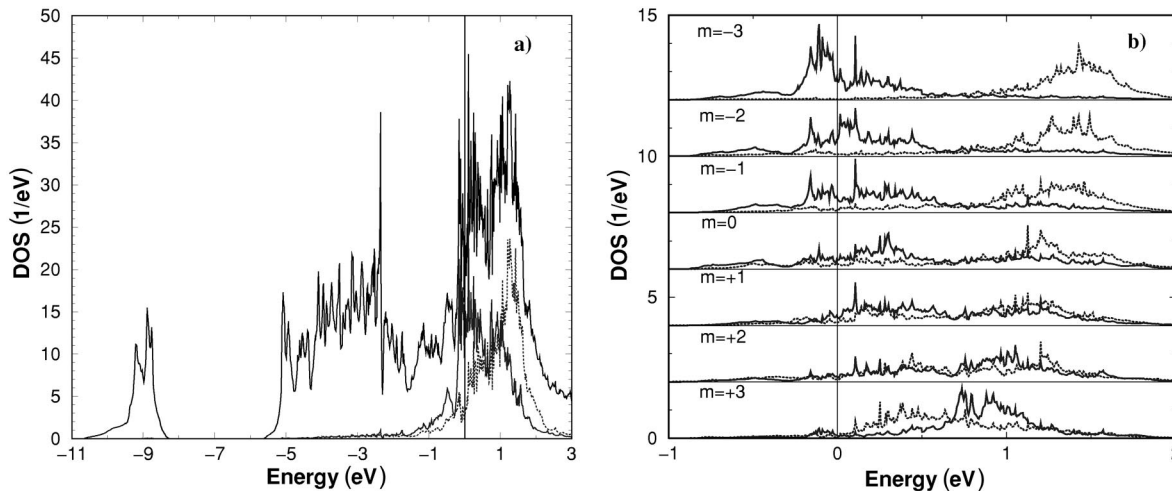


FIG. 3. (a) Total and U-atom 5f DOS; (b) U-atom 5f partial DOS resolved according to m_l for \uparrow (full line) and \downarrow (dotted line) components of spin.

can also cause the reduction of the calculated static magnetic moment and improve agreement with the experiment.⁸

The LSDA calculations often fail to reproduce the magnetic properties of f -electron materials due to oversimplified treatment of correlation effects. We attempt to improve the LSDA by using the LSDA+Hubbard U (LSDA+ U) approach.^{3,17} In these calculations, the atomiclike exchange $J=0.3$ eV constant is chosen for the U atom,¹⁸ and Hubbard U is varied as a parameter from zero up to 1 eV. The calculated total magnetic moment $M_J=M_s+M_l$ is then varied from $0.575\mu_B$ ($U=0$) to $1.29\mu_B$ ($U=1$ eV), exceeding the experimental value of $0.42\mu_B$. The experimental magnetic moment can be reproduced for an unphysical negative value of U only. It indicates that the LSDA+ U does not have an advantage over the conventional LSDA for URhGe, due to the itinerant nature of its f electrons, and the quantitative improvement over the LSDA can be expected in the dynamical mean-field theory.¹⁹ Still, the LSDA theory is shown to

perform reasonably well for URhGe as compared with the experimental data.

To summarize, LSDA calculations are shown to provide a consistent picture of the electronic and magnetic character of URhGe that is essential for understanding the coexistence of superconductivity with strong ferromagnetism. The calculations show that URhGe is the easy b - c -plane ferromagnet with the c easy magnetization axis. When U-atom spin magnetic moments are ferromagnetically ordered along the c easy axis, there is AFM ordering of the orbital magnetic-moment components along the a axis yielding a noncollinear magnetic structure in the a - c plane. We did not consider here the noncollinear spin arrangement, which is also possible and is the subject of further investigation.

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¹³The reduced symmetry $\{E, I\}$ keeps the same number of G stars and nonspherical muffin-tin components in the full-potential expansion for all three directions of the spin magnetization.

¹⁴In these calculations the spin magnetic moments on U atoms are fixed to be collinear.

¹⁵For the small rotation angles, the calculations become more difficult than for the total MAE itself, which is about one hundred times bigger than the small rotation angle total-energy difference.

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