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Electronic structure and magnetism of antiferromagnetic heavy fermion compound YbSi

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Abstract

The electronic properties of YbSi are studied by band structure calculation based on the density functional theory within the LDA, LDA + U, and the fully relativistic scheme. When the Coulomb potential is added to the Yb 4f orbitals, the degeneracy between the different f orbits would be lifted and they are split into lower Hubbard bands and upper Hubbard bands. The fully relativistic band structure scheme shows that spin–orbit coupling splits the 4f states into two manifolds, the $4f_{7/2}$ and the $4f_{5/2}$ multiplet.

1. Introduction

The strongly correlated electron systems have been attractive in condensed matter physics in recent years, in particular heavy fermion (HF) metals, which are close to a magnetic quantum critical point (QCP). This is due to the fact that such systems develop low temperature thermodynamic, transport and magnetic properties that deviate from the conventional Landau Fermi liquid (LFL) theory. The most interesting is that the ground state properties can be tuned around a magnetic QCP by a control parameter such as pressure, magnetic field or doping [1]. At present, an increasing number of examples of Ce and U based systems such as $CeCu_{6-x}$, $CePd_2Si_2$, and $CeIn_3$ have been found to exhibit magnetic quantum criticality by either doping- or pressure-tuning [2–4]. Heavy fermion systems are characterized by a large effective quasiparticle mass as reflected in strongly enhanced electronic specific heat coefficient and spin susceptibility at low temperature. The heavy fermion systems have a large Pauli susceptibility at low temperature as a consequence of the large density of states. The temperature dependence of C and χ can be explained in terms of narrow resonant levels of a narrow band with a typical width of 1 meV or so. The narrow peak in the density of states has been attributed to the Kondo effect, but its formation is still unknown. The investigation of Yb-based compounds with anomalous magnetic behaviour is particularly interesting. They show a quite large variety of exciting properties, such as heavy fermion behaviour or anomalous magnetism. In the Yb-based compounds, the instability of the f shell of this element allows them to be tuned from a magnetic to a nonmagnetic state by changing the chemical composition or by applying pressure. At the crossover from the nonmagnetic to the magnetic state, one observes unusual properties

such as the formation of heavy fermions, the onset of unconventional superconductivity or strong deviation from the Fermi-liquid behaviour usually expected in a metal.

Among them, the YbSi low temperature specific heat experimental data shows that the cusp of the zero-field specific heat at 1.6 K indicates a phase transition, probably of an antiferromagnetic nature [5, 6]. This was confirmed by the field dependence of the transition, since both the Néel temperature and the height of the cusp are reduced by an applied magnetic field. The presence of antiferromagnetic spin waves gives rise to a large βT^3 term in the specific heat at low temperature, in addition to an electronic contribution γT. A large part of the low temperature C/T can be attributed to a narrow peak at the Fermi level. The decrease of C/T as one increases the temperature above 2 K can be interpreted in terms of an $S = \frac{1}{2}$ Kondo resonance. For spin larger than $\frac{1}{2}$ the Coqblin–Schrieffer model predicts a Kondo resonance centred above the Fermi level, not at the Fermi energy. As a consequence, C/T for $S > 1$ first increases as T increases. The nature of this decrease of C/T for YbSi is qualitatively different and leads to the fact that the $S = \frac{7}{2}$ Hund's rule ground multiplet of Yb is quenched into a doublet by crystalline fields. The existence of a sizable crystal-field splitting is supported by a upturn of C/T versus T^2 between 10 and 20 K, which is believed to be a precursor to an excited crystal-field level. And the susceptibility of YbSi for high temperature data shows a Curie–Weiss behaviour with an antiferromagnetic moment of 4.21 μ_B and a Curie–Weiss temperature of about 40 K. The magnetic moment is smaller than the saturation value of Yb^{3+}, which has a value of 4.54 μ_B. The resistivity of YbSi above 25 K is unusually high for a metal and approximately constant. Its value is about eight to ten times larger than the resistivity of other Ce or U based heavy fermion systems. In stoichiometric heavy fermion compounds the resistivity initially increases as one lowers the temperature T, then goes through a large maximum and shows a sharp decrease at very low T. Both features, the existence of a maximum and the high resistivity at this maximum, are uncommon to normal metals. The rapid decrease of the resistivity at low temperature is caused by a transition from incoherent to coherent scattering of the conduction electrons by the rare-earth ions.

In this work the precise self-consistent full potential local orbital minimum basis band structure scheme (FPLO) is employed to investigate the electronic and magnetic properties of YbSi based on the density functional theory. We consider the effect of magnetism on the electronic band structure and compare with experiments.

2. Crystal structure and method of calculations

YbSi belongs to the orthorhombic CrB-type crystal structure ($Cmcm$ space group) with both Yb occupying the 4c site (mm site symmetry) and Si the 4c site (mm site symmetry). We used the experimental lattice constants $a = 4.18$ Å, $b = 10.31$ Å and $c = 3.77$ Å. There are two formula units in a primitive cell.

We have applied the full-potential nonorthogonal local-orbital minimum-basis (FPLO) scheme within the local density approximation (LDA) [7]. In these scalar relativistic calculations we used the exchange and correlation potential of Perdew and Wang [8]. Yb 4s, 4p, 4d, 4f, 5s, 5p, and Si 2s, 2p states were included as valence states. All lower states were treated as core states. We included the relatively extended semicore 4s, 4p, 4d, 4f states of Yb as band states because of the considerable overlap of these states on nearest neighbours. This overlap would be otherwise neglected in our FPLO scheme. Yb 6p states were added to increase the quality of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential $(r/r_0)^4$, was optimized to minimize the total energy. The self-consistent potentials were carried out on a k mesh of 12 k points in each direction of the Brillouin zone, which corresponds to 301 k points in the irreducible zone.

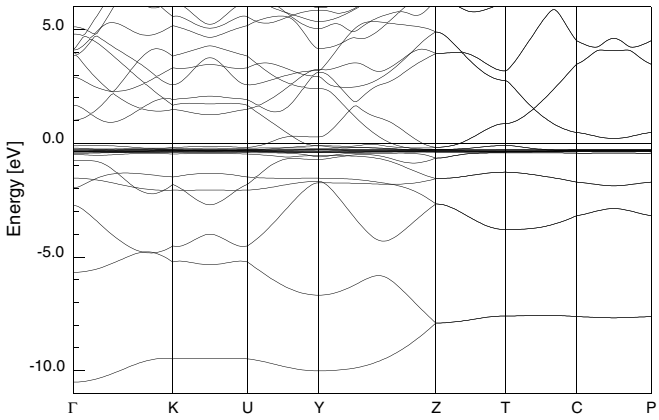

Figure 1. The full band structures of YbSi along symmetry lines.

3. Results

We first discuss the band structure results from the conventional theoretical methods in the local density approximation. The full band structure of YbSi is shown in figure 1. The Si 3s and 3p states spread over the range between -11 and -0.5 eV. Just below the Fermi level the Yb 4f states are dominant with very flat bands (bandwidth is about 0.1 eV). Above the Fermi energy there are varying amounts of Yb 6s, 5d and Si 3s, 3p states. At Y and Z points Yb 5 $d_{x^2-y^2}$ lies at 0.2 eV above the Fermi level and disperses downward across the E_F. We also study the on-site atomic-like correlation effects beyond LDA by using the LDA + U approach in a rotationally invariant, full potential implementation [9]. Minimizing the LDA + U total energy functional with spin orbit coupling (SOC) treated self-consistently [10] generates not only the ground state energy and spin densities, but also effective one-electron states and energies that provide 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. The Coulomb potential U and the exchange coupling J for the Yb 4f orbitals have been chosen to be 7.0 and 0.68 eV respectively. The band structure calculated within the LDA + U scheme is shown in the middle panel of figure 2. We observe that the crystal field splittings of Yb 4f bands within LDA are quite small and in fact difficult to identify due to hybridization with itinerant bands. From LDA + U, the 4f bands are still very flat but are split into two manifolds (at -0.85 and -1.2 eV) by some combination of the crystal field and the anisotropy of the U interaction by a total 0.35 eV. We also calculated fully relativistic band structure to see the spin–orbit coupling effects. The result is shown in the bottom panel of figure 2. As you see, the spin–orbit interaction splits the 4f states into two manifolds, located 0.2 and 1.5 eV below the Fermi level, which are the $4f_{7/2}$ and the $4f_{5/2}$ multiplet respectively. The corresponding total electronic density of states with two strong peaks comes from the 4f states.

Density of states for the LDA, LDA + U, and fully relativistic calculation is shown in figure 3. Near the Fermi level the main contribution is the Yb 4f states. The very flat Yb f bands make a high peak in the density of states 0.4 eV below Fermi level in the LDA calculation. We can observe the two splittings at -0.85 and -1.2 eV in the LDA + U calculation. We can also observe the two manifolds in the fully relativistic scheme.

The calculated magnetic moment of YbSi within the LDA scheme is 0.215 μ_B/f.u. (where f.u. means formula unit). It is mainly from the Yb-derived 4f orbitals. When the on-site

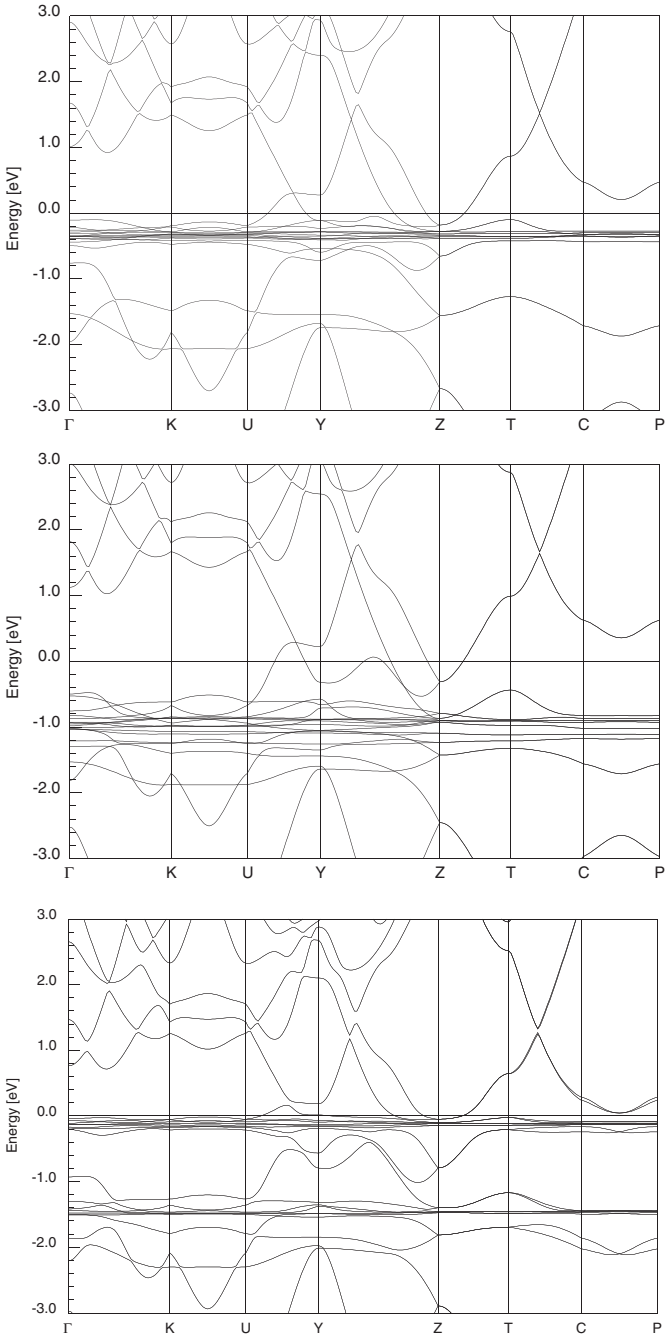

Figure 2. Top panel: the blow-up LDA band structure of YbSi. Middle panel: the LDA + U scheme band structure of YbSi. Bottom panel: the fully relativistic band structures of YbSi near the Fermi level. We can see the Yb 4f splitting due to the spin–orbit coupling. The splitting is about 1.3 eV.

correlation potential is added to the Yb 4f electron, the degeneracy between the different f orbits would been lifted and the Hund's rules dominate the locally occupied 4f electrons, which

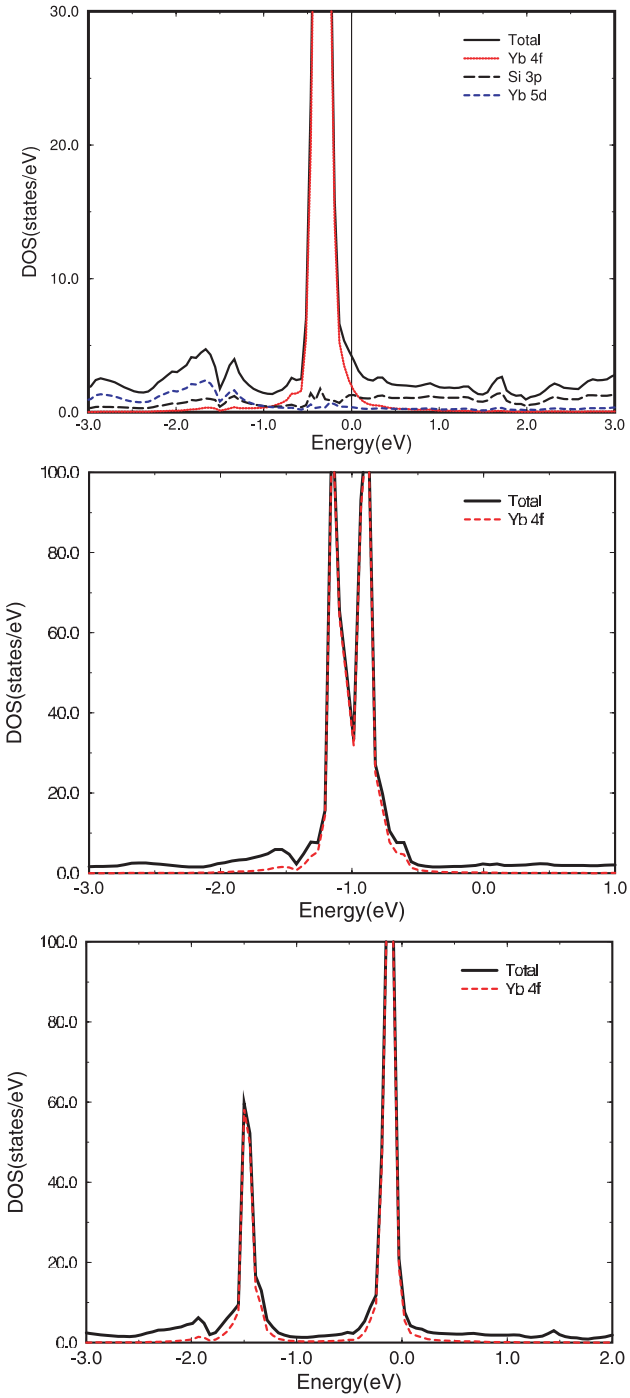

Figure 3. The density of states of YbSi. Top panel: DOS of the LDA; the Yb 4f bands dominate the states near the Fermi level. Middle panel: DOS of LDA + U; the 4f bands split into two manifolds. Bottom panel: showing the spin–orbit coupling effects of fully relativistic calculation. The splitting is about 1.3 eV.

(This figure is in colour only in the electronic version)

yields the total magnetic moment 0.202 μ_B. With a fully relativistic scheme we calculated a magnetic moment of value 0.208 μ_B. Bonville *et al* reported that the Mössbauer data confirm the presence of magnetic ordering below 1.6 K and show that the spontaneous moment of the Yb^{3+} ion is 0.2–0.3 μ_B [6].

Density functional calculations are very reliable in calculating the instability to ferromagnetism. The presence of an electronic instability is signalled by a divergence of the corresponding susceptibility. In the following we study the uniform magnetic susceptibility using the method of Janak [11]. The uniform magnetic susceptibility of a metal can be written as

$$\chi = \frac{\chi_0}{1 - N(E_F)I}, \tag{1}$$

where the numerator stands for the Pauli susceptibility of a gas of non-interacting electrons proportional to the density of states at the Fermi level $N(E_F)$, and the denominator represents the enhancement due to electron–electron interaction. Within the Kohn–Sham formalism of density functional theory the Stoner parameter I is related to the second derivative of the exchange–correlation functional with respect to the magnetization density. We have evaluated, within the density functional theory formalism, the Stoner enhancement of the susceptibility $\chi = \frac{\chi_0}{1-IN(E_F)} \equiv S\chi_0$, where $\chi_0 = 2\,\mu_B^2 N(E_F)$ is the non-interacting susceptibility and S gives the electron–electron enhancement in terms of the Stoner constant I. We have calculated I using both the Janak–Vosko–Perdew theory [11] and fixed spin moment calculations [12]. The calculated density of states and Stoner parameter I gives $IN(E_F) \sim 0.6$, smaller than unity, which does not show a ferromagnetic instability.

A heavy fermion compound is characterized by a larger electronic specific heat coefficient γ. YbSi is a heavy fermion compound with $\gamma = 900$ mJ K^{-2} mol^{-1}. The large specific heat coefficient of the YbSi compound could not be yielded by our band calculation. This can be seen from the calculated electronic structure. It can be found that the total DOS at the Fermi level is about 2.06 states eV^{-1}, which corresponds to $\gamma_b = 4.82$ mJ K^{-2} mol^{-1} and underestimates the experimental value by a factor of 186.7. The discrepancy between the band calculation and experiment for specific heat coefficient is attributed to the formation of quasiparticles. There is exchange interaction J between the local f and the conduction electrons in YbSi. The ground state of the Yb compound is determined by the competition of the Kondo and indirect RKKY interaction. With a large J, the Kondo coupling becomes strong and the system located at the borderline of the magnetic–nonmagnetic transition. The exchange interaction between the local f electron and the conduction electrons will result in the formation of the quasiparticle. It has a larger mass compared with the bare electron and the enhancement of mass increases with the increase of exchange. Because of the volume contraction, the exchange interaction between the f and the conduction electrons is large in YbSi. This will result in the f electrons behaving like itinerant electrons and the narrow f bands being located at the Fermi level. On the other hand, when the exchange interaction between f and conduction electrons is smaller, the occupied 4f orbitals are located near the Fermi level while the unoccupied 4f orbitals are at the conduction bands. The quasiparticle mass is appropriate to the DOS at the Fermi level. So the quasiparticle mass is greatly enhanced in YbSi. Indeed, it has been shown that when the Yb 4f electrons in YbSi are treated as localized electrons the quasiparticle mass is enhanced over the band calculation by a factor of 186.7.

4. Summary

In this paper we studied the electronic band structure with three different schemes. In each case the 4f bands lie near the Fermi level. This shows that the Coulomb potential on Yb 4f orbitals

and spin–orbit interaction is a key factor to understand the electronic and magnetic properties of YbSi. When the Coulomb potential is added to the Yb 4f orbitals, the degeneracy between the different f orbits would be lifted and they are split into lower Hubbard bands and upper Hubbard bands. The exchange interaction between local f electrons and conduction electrons plays an important role in their heavy fermion characters. Moreover, the fully relativistic band structure scheme shows that spin–orbit coupling splits the 4f states into two manifolds, the $4f_{7/2}$ and the $4f_{5/2}$ multiplet.

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