Electronic structure analysis of UIr using soft x-ray photoemission spectroscopy and band calculation

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Abstract. Uranium ferromagnet UIr is well-known to a pressure-induced superconductor without an inversion symmetry. In order to clarify the U ⁵f states of ferromagnetically-ordered UIr below Tc ∼46 K and at ambient pressure, we observed ⁵f-sensitive soft X-ray photoemission spectra (SXPES), and calculated the band structure by a relativistic LAPW method in a local-spin density approximation. The temperature-dependent angle-integrated SXPES near the Fermi energy show a definite energy-shift of the band structures below and above Tc. The exchange splitting of the ⁵f bands seems to be consistent with an itinerant band picture like Stoner model. Furthermore the angle-resolved SXPES are compared with the theoretical band structure to investigate the relationship between the band shift and the magnetism.

Heavy-fermion superconductivity in the noncentrosymmetric crystal structure is a great issue that needs to be solved experimentally and theoretically in f-electron systems: The noncentrosymmetric superconductor CePt₃Si (Tc ∼0.75 K) [¹] has been first announced, and around the same time a pressure-induced superconductivity was reported in UIr of the monoclinic PbBi-type structure [²], and then also in CeRhSi₃ [³], CeIrSi₃ [⁴] and CeCoGe₃ [⁵] of the BaNiSi₃-type cerium compounds. The loss of the inversion symmetry brings out the Rashba interaction, causing a spin-orbit-like splitting into the electronic structure and creating two Fermi surfaces with a similar shape, but with each different direction of spins. In the superconducting state, it is theoretically suggested that a Cooper pairing is formed from a coupling between the spins on the Fermi surfaces, resulting in an order parameter mixed up with spin-singlet and triplet states, which are unconnected in the usual superconductors. Accordingly it is of great interest to investigate how the electronic structure and Fermi surface are in such system.

In the noncentrosymmetric system UIr is one of the ferromagnetic uranium compounds. The primitive monoclinic crystal structure of UIr belongs to space group P2₁ and contains eight U and Ir atoms each in the unit cell. The lattice constants are a=5.62 Å, b=10.59 Å and...
Figure 1. (a) Angle integrated photoemission spectrum of UIr observed with the photon energy of 425 eV at 20 K (red line) and theoretical density of states evaluated from LDA band calculation (blue line). (b) Temperature dependence of AIPES near the Fermi level.

c=5.60 Å with $\beta=98.9^\circ$ [6]. The magnetic properties show an Ising-like character with the Curie temperature of $T_{c1} \sim 46$ K at ambient pressure and the magnetic moment is oriented along the [101] direction. The magnetic susceptibility follows the Curie-Weiss law with an effective moment 2.4 $\mu_B$/U, while the ordered moment is 0.5$\mu_B$/U in the ordered state, showing an itinerant feature of U-$5f$ electrons. In the high pressure experiment [7] the ferromagnetic phase FM1 with $T_{c1} \sim 46$ K at ambient pressure disappears around 1.7 GPa and the different ferromagnetic phases FM2 and FM3 with a small moment of 0.05 $\mu_B$/U emerge in the pressure ranges of $P_{c1} < P < P_{c2} = 2.1$ GPa and $P_{c2} < P < 2.74$ GPa, respectively, in the low temperature. In the FM3 phase the superconducting phase comes into existence around 2.6 GPa [8]. It is pointed out that the superconductivity is closely linked with the ferromagnetic quantum criticality.

The photoemission spectroscopy (PES) technique is a very powerful tool to examine the electronic states in strongly correlated electron systems: In the soft x-ray region angle-resolved and photo-tuning photoemission spectra can be measured to identify a bulk U-$5f$ band dispersion along all the directions of wave vectors in the Brillouin zone [9] by considering some significant advantages in a bulk sensitivity of soft x-ray photons to the penetration depth and $5f$-dominating effect of photoionization cross-section. Temperature dependence of the angle-resolved photoemission spectra (ARPES) highlights the energetic and dispersive shifts of the U-$5f$ bands regarding the magnetic ordering and/or the volume change. In UPd$_2$Al$_3$ it was detected that the itinerant U-$5f$ bands across the Fermi energy ($E_F$) at 20 K are transfigured drastically into the localized levels shifted down away from $E_F$ at 100 K [10].

In a purpose of the paper we clarify the $5f$-derived electronic structure in the ferromagnetically-ordered UIr below $T_{c1} \sim 46$ K at ambient pressure using soft x-ray PES (SXPES) measurement and an analysis by means of a relativistic LAPW (RLAPW) method [11] within a local density approximation (LDA). Figure 1(a) shows the angle-integrated photoemission spectra (AIPES) of UIr observed with the photon energy of 425 eV at 20 K below $T_c$ by red line and the theoretical density of states evaluated from the LDA band calculation by blue line. For the AIPES measurements the energy and the angle resolution were about 70 meV and $\pm 0.15^\circ$, respectively and the AIPES were obtained by angular integration between $\pm 5^\circ$ in the [101] direction. The origin of the energy is set at $E_F$ in the unit of eV, thereafter and the AIPES with positive binding energies demonstrate the occupied states of valence bands in UIr.
Figure 2. (a) Angle-resolved photoemission spectra of UIr for the paramagnetic state at 120 K in red lines and ferromagnetic state at 20 K in blue lines observed around the Γ point in the [101] direction. (b) The Brillouin zone corresponding to the monoclinic crystal structure of UIr. (c) Theoretical band structure of UIr along the Γ-D line in a local-density approximation.

Here we can see a peak structure in the vicinity of $E_F$, gradually dropping down to 1 eV without other peak structures, and then increasing abruptly with valence states distributing widely from 1 eV to 6 eV. The findings of the LDA band calculation and the systematic change of the AIPES as a function of photon energy explain that the peak structure around $E_F$ is composed mainly of the U-5$f$ bands and that the wide valence states centering at 3 eV correspond to the Ir-5$d$ bands. Comparing the experimental AIPES with the theoretical result in Fig. 1(a), the shape of the U-5$f$ AIPES, existing just below $E_F$, indicates that the U-5$f$ electrons of UIr form itinerant bands in the ferromagnetic state.

In Fig. 1(b) we depict the temperature dependence of the AIPES at 20 K (brown) and 35 K (red) below $T_{c1}$ and at 60 K (green) and 120 K (blue) above. Here note that the energy range is more limited around $E_F$ than that of Fig. 1(a). It turns out that the peak position of the AIPES around 50 meV are gradually raising up as the temperatures are going down, while the density of state at $E_F$ is decreasing. In view of this it is possibly interpreted that the U5$f$ bands existing around $E_F$ are shifted by an exchange splitting like the Stoner model of an itinerant magnetism, in the same manner as ferromagnet UTe [12].

Figure 2(a) shows angle-resolved photoemission spectra (ARPES) of UIr for the paramagnetic (PM) state at 120 K in red lines and for the ferromagnetic (FM) state at 20 K in blue lines, observed along the Γ-D lines in the [101] direction in the Brillouin zone (BZ). Figure 2(b) indicates the monoclinic BZ in UIr as well as the measured [101] direction by arrow. As seen in Fig. 2(a), there appears the difference between the PM and FM states also in the ARPES. The difference can be found out that a band with parabolic dispersion is at the center of the Γ point.
along the D-Γ-D line as indicated by a broken line, although it is a little bit hard to be discernible to the eyes. On the broken line, the change of the ARPES from the paramagnetic state to the ferromagnetic state is reasonably large, thus expecting the existence of the U5f-rich bands along this curve. If the positions of each parabolic-like bands of the PM and FM states are traced by fitting analyses with the Gaussian functions to the ARPES normalized along the momentum (or wave number) direction, the shift value between the PM and FM bands is estimated as 50 meV at a maximum.

The theoretical band structure of UIr along the Γ-D line, calculated by the RLAPW method in the LDA, is given in Fig. 2(c). The red- and blue-coloring represent the strength of the selected contribution for the U-5f and Ir-5d orbitals, respectively. The U-5f bands are located above the binding energy of 0.5 eV and the dispersive Ir-5d bands exist below around 1.5 eV. In intermediate range of the binding energies the hybridized and/or mixed bands with large bandwidth consist chiefly of the U-5f and the Ir-5d states. A remarkable point is that the U-5f bands with a parabolic dispersion appear starting at center of the Γ point around 0.5 eV, as shown by a broken line colored in Fig. 2(c). Judging from a comparison of the measured (Fig. 2(a)) and the calculated (Fig. 2(c)) results, it seems that the parabolic bands of the ARPES originates from the U-5f bands as predicted above and additionally gives a strong contribution to the magnetic properties in point of the energy shift.

The electronic specific heat coefficient is evaluated as $\gamma_b = 19.8 \text{ mJ/(K}^2\text{ mol)}$ from the density of states obtained in the LDA band calculation. The experimental one is obtained as $\gamma = 48.5 \text{ mJ/(K}^2\text{ mol)}$ and this $\gamma$ value is suggested to be consistent with the large cyclotron mass of de Haas-van Alphen effect [6]. The enhancement factor $\lambda = \gamma / \gamma_b - 1$ due to the electron correlation is estimated as a small value of 1.4, and therefore the LDA band calculation might be not so bad as a starting analysis to the electronic structure of UIr as well as other uranium compounds with a moderately heavy effective mass.

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