

High-Resolution Photoemission Study of UNi₂Al₃ and URu₂Si₂

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High-resolution low-temperature photoemission spectroscopy has been performed for UNi₂Al₃ and URu₂Si₂ to study the nature of 5*f* electrons in U-based heavy fermion materials. Photoemission spectra of both compounds have a sharp peak at E_F and a large broad peak around 2 eV, while only UNi₂Al₃ exhibits an additional small broad feature at 0.6 eV. The two features in the vicinity of E_F (the E_F -peak and the small structure at 0.6 eV) are found to have a dominant U 5*f* character while the prominent peak around 2 eV is due to the Ni 3*d* or Ru 4*d* states. Comparison with the band structure calculations and experimental results on UPd₂Al₃ suggests that the E_F -peak is ascribed to itinerant U 5*f* electrons while the following broad feature at 0.6 eV represents localized *f* electrons.

KEYWORDS: high-resolution photoemission spectroscopy, uranium compounds, 5*f* electrons, electronic structure

§1. Introduction

U-based compounds have attracted much attention owing to a variety of unique properties. For example, some of them possess itinerant electron characters (Pauli paramagnetism, superconductivity) while others show spin fluctuation as well as local moments with magnetic ordering. Recently several U-compounds were found to behave as a heavy-fermion system,¹⁾ which has an electronic specific heat coefficient much larger than those of simple metals and shows anomalous magnetic susceptibility. Discovery of the coexistence of the superconductivity and antiferromagnetic ordering in U-based heavy fermion systems²⁻⁴⁾ suggests a novel superconducting electron-electron pairing mechanism such as the two-channel Kondo model,⁵⁾ and the *d*-wave symmetry has been proposed for the superconducting order parameter.^{6,7)} Although the coexistence of superconductivity and long-range antiferromagnetic order has been already observed in RMo₆S₈, RMo₆Se₈, and RRh₄B₄ (*R* = rare earths),⁸⁾ it has been generally accepted that the superconductivity and the long-range magnetic order originate in different electrons; the former is associated with the transition metal *d*-electrons while the latter stems from the localized 4*f* electrons of rare earth ions.⁹⁾ On the other hand, U 5*f* electrons in recently discovered U-based heavy fermion superconductors, UPd₂Al₃, UNi₂Al₃, and URu₂Si₂,²⁻⁴⁾ appear to be associated directly with both superconductivity and long-range magnetic ordering.

In this paper, we report a high-resolution photoemission (HR-PES) study on UNi₂Al₃ and URu₂Si₂. It is well established for Ce compounds that a photoemission spectrum is dominated by many-body effects, as is well described with the single-ion Kondo model based on the Anderson Hamiltonian.¹⁰⁾ But it is unclear that the single-impurity model is applicable to U-based heavy

fermion systems because the Coulomb interaction between 5*f* electrons is considerably reduced and the spatial distribution of 5*f* electrons is more extent than that of Ce 4*f* electrons. In order to study the nature (itinerant or localized) of U 5*f* electrons in U-based heavy fermion superconductors, we measured HR-PES spectra near E_F of UNi₂Al₃ and URu₂Si₂ and compared them with the band structure calculations as well as our previous photoemission results on UPd₂Al₃.¹¹⁾ We also studied the temperature-dependence of the spectra to obtain an additional insight to the character of the electronic states near E_F .

§2. Experimental

Single crystals of UNi₂Al₃ and URu₂Si₂ were prepared in a tri-arc furnace by the Czochralski pulling method. We checked the crystal structure and its single-crystallinity by X-ray diffraction; UNi₂Al₃ shows the hexagonal PrNi₂Al₃ structure with lattice parameters of $a = 5.207 \text{ \AA}$ and $c = 4.018 \text{ \AA}$, while URu₂Si₂ possesses the body-centered tetragonal ThCr₂Si₂ structure with lattice parameters of $a = 4.124 \text{ \AA}$ and $c = 9.582 \text{ \AA}$.

Photoemission measurements were carried out with a home-built high-resolution photoemission spectrometer with a VSW 300 mm-diameter hemispherical electron energy analyzer and a brilliant discharge lamp. The base pressure was 3×10^{-11} Torr. The energy resolution was 30/35 meV for He I (21.2 eV)/He II (40.8 eV) measurements. Single crystals were scraped *in-situ* by a diamond file to obtain a clean surface for photoemission measurements. Since we observed degradation of the sample surface as being evident by a gradual growth of an additional feature at a binding energy of 10 eV after an hour, we repeated scraping every 10 min and obtained a final spectrum with a good signal-to-noise ratio by adding each scans. The Fermi level of the sample was referenced to that of a gold film deposited on the sample substrate and

its position was accurate to better than ± 2 meV.

§3. Results and Discussion

Figure 1 shows the valence band photoemission spectra of UNi_2Al_3 measured with He I and He II resonance lines at 20 K. Both spectra are dominated by a broad peak at a 1.5–2.5 eV binding energy, which is ascribed to the Ni 3*d* states. Comparing with UPd_2Al_3 ,¹¹⁾ it is found that the *d* band width is narrower in UNi_2Al_3 . This is well explained in terms of the difference of the number of *d* electrons and the stronger localized character of 3*d* electrons compared with that of 4*d* electrons. We find that the photoemission intensity near E_F is enhanced in the He II spectrum compared with the He I, which suggests that the features near E_F have a dominant U 5*f* character because the difference in the photoionization cross-section between He I and He II is larger for U 5*f* electrons than for electrons in the other orbitals in the compound.¹²⁾

The sharp peak at E_F may be associated with the many-body effect via Kondo-type screening from the conduction band as predicted by the non-crossing approximation (NCA) calculation.¹³⁾ But we find that the width of the peak at E_F (~ 200 meV) is considerably larger than that predicted from the NCA or Gunnarsson-Schönhammer (GS) calculation which is of the order of T_K (~ 10 meV). Imer *et al.*¹⁴⁾ argued that the multiplets or satellite structures near E_F may blur the sharpness of Kondo-resonance peak or a strong hybridization may move the Kondo peak away from E_F . All these effects reduce the spectral intensity of the occupied part of Kondo peak and simultaneously increases its width.

In order to study the U 5*f* states near E_F more in detail, we subtracted the He I spectrum from the He II spectrum according to the procedure employed in previous studies,^{11, 14)} since the relative difference of photoionization cross-section between He I and He II excitations is remarkably large for U 5*f* electrons compared with those of electrons in other orbitals in the compounds¹²⁾ and the subtracted spectrum mostly represents the U 5*f* states. The difference spectrum after subtraction is shown in Fig. 2 together with the calculated U 5*f* partial density of states.¹⁵⁾ As is found in Fig. 2, the difference spectrum exhibits a narrow peak at E_F and a following broad hump around 0.6 eV. We find that the calculated partial U 5*f* DOS shows a fair agreement with the difference spectrum; it has a relatively sharp structure at E_F and a broad tailing toward the high binding energy. However, we notice that the intensity around 0.6 eV is obviously higher in the photoemission spectrum than in the calculated DOS when we normalize the intensity at the narrow peak at E_F . This may suggest a certain contribution from the many-body effect to the photoemission spectrum. We have observed a similar two-peaked structure in the near- E_F photoemission spectrum of UPd_2Al_3 ,¹¹⁾ where we have ascribed the E_F -peak and the broad hump at 0.6 eV to “itinerant” and “localized” parts of the U 5*f* states, respectively. The same interpretation is applicable to UNi_2Al_3 since the photoemission-spectral feature looks very similar. In this scenario, the localized U 5*f* states contribute mainly to formation of the localized

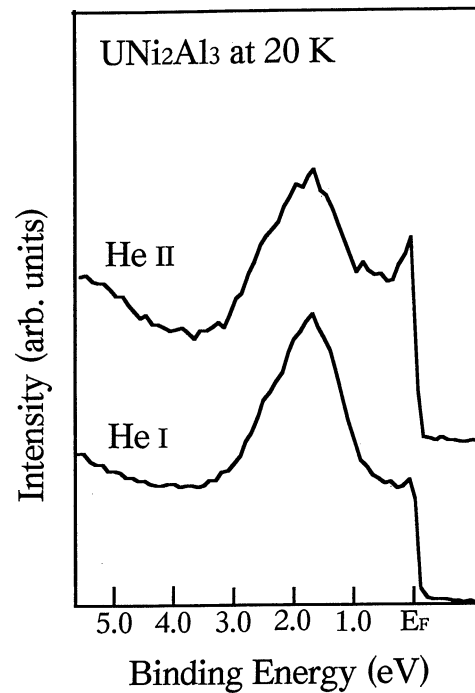


Fig. 1. Valence-band photoemission spectra of UNi_2Al_3 measured at 20 K with He I (21.2 eV) and He II (40.8 eV) resonance lines.

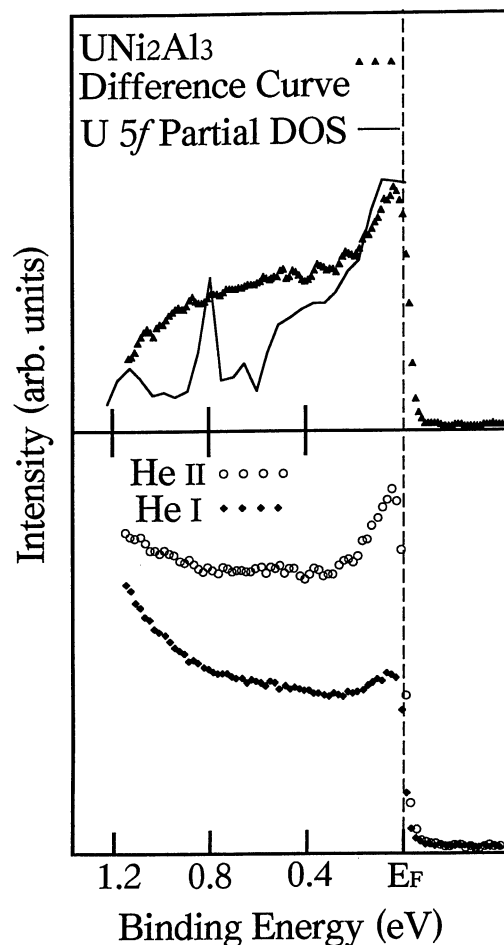


Fig. 2. High-resolution photoemission spectra near E_F of UNi_2Al_3 measured at 20 K with He I and He II photons (lower panel). The intensity is normalized at 1.2 eV binding energy. In upper panel, the difference spectrum (He II–He I) is compared with the calculated U 5*f* partial DOS.¹⁵⁾

magnetic moment while the itinerant U $5f$ states at E_F play a role in superconducting pairing. This scenario seems to have a strong physical reasoning because the Ni $3d$ band makes little contribution to localized magnetic moments and itinerant f electrons are unable to form a local magnetic moments by compensation theorem.¹⁶⁾ Moreover it is known that UNi_2Al_3 shows a competition between the RKKY interaction and the Kondo-singlet screening; this suggests that UNi_2Al_3 is located near the boundary in the Doniach phase diagram,¹⁷⁾ for which the existence of the localized f -character is essential.

Recently many efforts have been made to incorporate correctly the local electron correlation into the band structure calculation of uranium compounds. Actually, a recent advanced band calculation,¹⁸⁾ which includes the dynamic fluctuation around the local-density-approximation (LDA) electronic structure, has successfully explained the observed enhancement of the specific heat in UX_3 ($X=\text{Ir, Pt, Au}$) and its $5d$ -metal dependence. However, it is found that the calculated U $5f$ band is much narrower than that observed by combination of X-ray photoemission and Bremsstrahlung Isochromat spectroscopy (BIS).¹⁹⁾ Further, at least to our knowledge, there are no band structure calculations which successfully reproduce the two-peaked structure of the density of states near E_F in uranium compounds and the temperature variation of relative intensity as observed in UPd_2Al_3 .¹¹⁾

Figure 3 shows valence photoemission spectra of URu_2Si_2 at 20 K. Similarly to UNi_2Al_3 , a prominent broad feature is seen around 2 eV. It is ascribed to the Ru $4d$ states. Our high resolution He I spectrum is almost the same as that in the earlier work with $h\nu = 70$ eV by Grassmann.²⁰⁾ We find that the Ru $4d$ band is closer to E_F than the Ni $3d$ band in UNi_2Al_3 (see Fig. 1). This situation is favorable for stronger hybridization of the Ru $4d$ states with the U $5f$ counterparts at E_F in URu_2Si_2 , resulting in formation of mixed bands near E_F . In other words, U $5f$ electrons in URu_2Si_2 would have more extended character than those in UNi_2Al_3 . This conjecture is confirmed in Fig. 4, where the near- E_F photoemission spectra (He I, He II, and the difference spectra) of URu_2Si_2 are shown together with the calculated U $5f$ partial DOS.²¹⁾ The difference curve has a sharp peak at E_F and a broad tailing toward the high binding energy in good agreement with the band calculation. We find that the difference spectrum does not have a well-defined hump around 0.6 eV in contrast with that of UNi_2Al_3 (Fig. 2). Since the broad hump around 0.6 eV has been interpreted as "localized f states", the absence of the definite hump at 0.6 eV in the photoemission spectrum of URu_2Si_2 implies that U $5f$ electrons in URu_2Si_2 have a highly itinerant character than in UNi_2Al_3 . This is consistent with the experimental fact that URu_2Si_2 has smaller a localized moment ($\mu(\text{U}) = 0.04 \mu_B$) than that of UNi_2Al_3 ($\mu(\text{U}) = 0.1 - 0.2 \mu_B$).^{2,3)}

In order to obtain a further insight to the nature of the electronic states near E_F , we measured temperature-dependence of HR-PES of URu_2Si_2 as shown in Fig. 5. We find that the spectrum shows almost no change except for the slope of the Fermi-edge cutoff. By a numer-

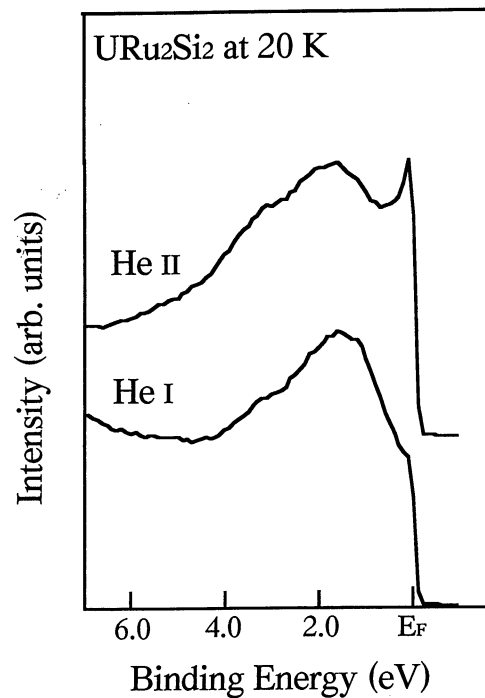


Fig. 3. Valence-band photoemission spectra of URu_2Si_2 measured at 20 K with He I (21.2 eV) and He II (40.8 eV) resonance lines.

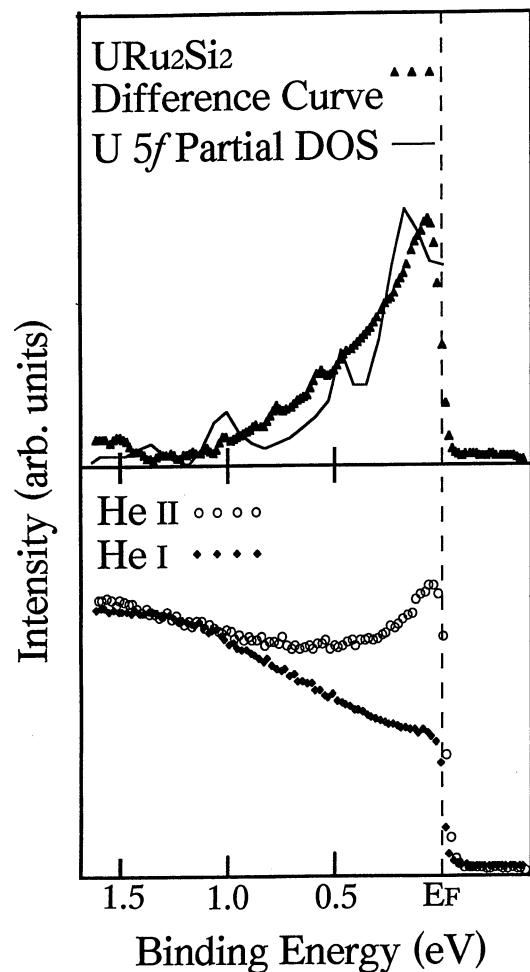


Fig. 4. High-resolution photoemission spectra near E_F of URu_2Si_2 measured at 20 K with He I and He II photons (lower panel). The intensity is normalized at 1.2 eV binding energy. In upper panel, the difference spectrum (He II-He I) is compared with the calculated U $5f$ partial DOS.¹⁹⁾

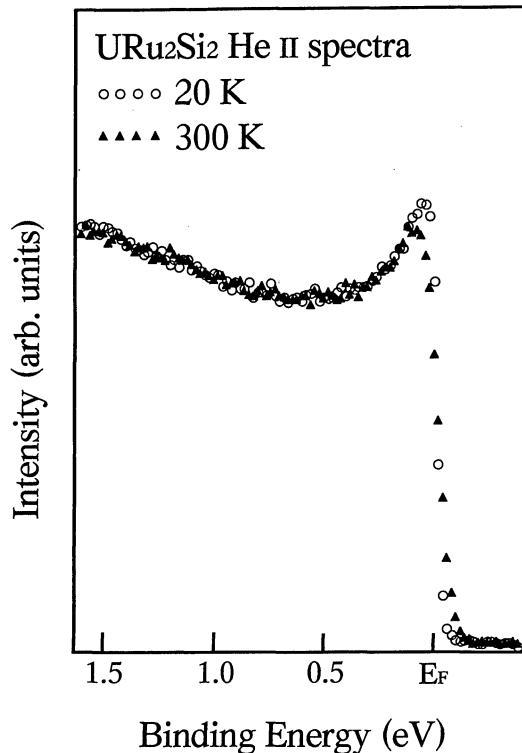


Fig. 5. High-resolution photoemission spectra near E_F of URu_2Si_2 measured with He II photons at two different temperatures (20 and 300 K) far below/above the Kondo temperature (~ 70 K).

ical simulation we found that this small change at E_F is well explained by thermal broadening of the Fermi-Dirac function at E_F . This also reinforces the above conclusion that the sharp peak at E_F is due to itinerant U $5f$ electrons as predicted from the band calculation, but is not produced via the many-body effect. Because, if the peak were associated with the Kondo resonance, the E_F -peak would show much drastic change with temperature since the measurement was carried out at two temperatures (20 and 300 K) far below/above the Kondo temperature (T_K of $\text{URu}_2\text{Si}_2 \sim 70$ K).

We have discussed the nature of the electronic states near E_F of two uranium compounds, UNi_2Al_3 and URu_2Si_2 , through the occupied electronic states, since photoemission spectroscopy probes the occupied electronic states. In order to confirm the present interpretation, a high-resolution temperature-dependent BIS may be useful since it provides a complementary information on the unoccupied electronic states.

§4. Conclusion

High-resolution low-temperature photoemission spectra of two U-based heavy-fermion superconductors, UNi_2Al_3 and URu_2Si_2 , show characteristic spectral shapes representing the nature of U $5f$ electrons. Both compounds exhibit a prominent photoemission band around a binding energy of 2 eV, which is ascribed to the Ni $3d$ or Ru $4d$ states. In the near- E_F region, photoemission spectra of both compounds possess a sharp peak at E_F , while only UNi_2Al_3 shows an additional small hump around 0.6 eV. Photon-energy dependence of the spec-

tra indicates a dominant U $5f$ character for these two features near E_F . Comparison with the band structure calculations and experimental results for UPd_2Al_3 suggest that the E_F -peak is attributed to the "itinerant" U $5f$ states while the small hump at 0.6 eV being due to the "localized" U $5f$ states. This suggests that U $5f$ electrons in UNi_2Al_3 are more localized than those in URu_2Si_2 . This is consistent with experimental results for the localized magnetic moment concentrated on U sites. The f electrons with localized character are expected to contribute to the antiferromagnetic long range ordering mediated by conduction electrons which include itinerant f electrons (RKKY-type interaction). The experimental results suggest that an U-based heavy fermion superconductor with long-range magnetic order is described essentially within the framework of the energy band concept or at least the Anderson lattice band because the overlap of f orbitals or coherence is important in such a spatially dispersed f electron systems.

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