Absence of U 5*f* band states in resonant photoemission spectra of UPd₂Al₃

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The U 5f spectral weight of $U_xLa_{1-x}Pd_2Al_3$ ($x=0.1$, 0.25, 0.6, and 1.0) is obtained by the resonant photoemission spectroscopy (RPES), and is compared with the results of the band-structure calculations. We have found that the spectrum of UPd₂Al₃ ($x=1$) could not be reproduced by the calculated U 5f density of states in shape and position, even if the contribution from U 6d states is considered. Moreover, the essential spectral shape did not change until $x=0.1$, where most of the uranium atoms are substituted with lanthanum atoms. All these results indicate that the U 5f band states are not observed in the RPES spectrum of UPd₂Al₃, and the single site effects govern it. [S0163-1829(99)01215-1]

I. INTRODUCTION

Uranium compounds exhibit a rich variety of electrical and magnetic properties, due to their peculiar behavior of the U 5f states. Numbers of experimental and theoretical studies have been made on these compounds. However, it is still unclear which of the two approaches, of the localized 5f electrons or of the itinerant 5f electrons, supplies a better basis for the description of these compounds. An essential question is whether the band-structure calculation can be a good starting point for a description of their U 5f states. To understand this point, the photoemission experiments have been performed for many uranium compounds, and the obtained spectra have been compared with the results of the band-structure calculations.[1] In particular, the resonant photoemission spectroscopy (RPES) technique is widely employed to extract the contribution only from the U 5f states. With this technique, the U 5f difference spectra have been obtained by using different energy-dependent photoionization cross sections for the U 5f and conduction-band electron. For the itinerant 5f compounds, like UIr₃ or UC, it has been reported that the calculated U 5f density of states (DOS) matches with the U 5f difference spectra.[2,3] Meanwhile, the situation of the heavy-fermion (HF) uranium compounds is controversial since the obtained U 5f difference spectra do not match with the calculated U 5f DOS. One point of view is that the band-structure calculations is still a good starting point for their description, even though the entire spectrum is not reproduced by the calculation. Arko *et al.* suggested that these spectra are understood by a superposition of a well-screened peak, which is entirely consistent with calculated U 5f DOS, and a poorly screened satellite, which is located about 2–3 eV below the E_F.[1] On the other hand, an impor-

tance of the single site effects has been proved by the studies on dilute alloys. Kang *et al.* measured the RPES spectra of $U_xY_{1-x}Al_2$ for $x=1-0.02$ and found that the spectral shape is essentially identical for the dilution of uranium atoms.[4] Therefore, the validity of the band-structure calculation on the description of these spectra is still an open question.

In the present study, we demonstrate that the RPES spectrum of UPd₂Al₃ reflects the single site effect of uranium atom sties, and the band-structure calculation cannot be a good starting point for their description. UPd₂Al₃ is an HF uranium compound which has transition into an antiferromagnetic phase at $T_N=14$ K and into a superconducting phase at $T_c=2$ K.[5] The coexistence of large local moments (0.85 μ_B) and a superconducting state is one of the characteristics of this compound. Another important point of this compound is that the local-spin-density-functional (LSDF) calculations could very well reproduce the results of de Haas–van Alphen (dHvA) experiments and the magnitude of local magnetic moments.[6] Thus, an itinerant description of the U 5f electrons is strongly supported in this compound, and it is interesting to examine its validity in the photoemission spectrum. Ejima *et al.* have first measured the RPES spectra of UPd₂Al₃,[7] and then compared the obtained spectra with the result of the band-structure calculations.[3,6] It has been pointed out that the obtained U 5f difference spectrum does not match with the calculated U 5f DOS, while the calculated Pd 4d DOS matches very well with the off-resonance spectra, where the Pd 4d states dominate the spectrum. In these studies, however, detailed analysis on the U 5f difference spectrum has not been provided, and the origin of the disagreements is not discussed.

In the present study, we have further performed the RPES study on the dilute alloys $U_xLa_{1-x}Pd_2Al_3$ for $x=0$, 0.1, 0.25,

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0.6, and 1.0 to clarify the validity of the band-structure calculation on the RPES spectrum of UPd_2Al_3. The dilute alloys $U_xLa_{1-x}Pd_2Al_3$ have the same crystal structure of UPd_2Al_3, and the substitution of uranium atoms with lanthanum atoms in these alloys reduces the contribution from U 5f band states. To complement the photoemission study, we have measured the x-ray bremsstrahlung isochromat spectroscopy (X-BIS) spectrum of UPd_2Al_3 also. The BIS studies are especially important for the uranium compounds since most of the U 5f states are located in an unoccupied part.

II. EXPERIMENT

Single crystals of $U_xLa_{1-x}Pd_2Al_3$ for $x = 0.1$, 0.25, 0.6, and 1.0 were grown in a tri-arc furnace. The details for their preparation and characterization have been described elsewhere.[8,9] The RPES experiments were performed at BL-2 of the SOR-Ring, a 0.38 GeV electron storage ring at the Synchrotron Radiation Laboratory of the Institute for Solid State Physics, the University of Tokyo. Total resolution of about 0.7 eV was obtained. The samples were mechanically scraped in the preparation chamber under ultrahigh-vacuum (UHV) condition. The O 2p derived state was checked before and after the measurements at the photon energy of $h\upsilon = 32$ eV and no oxygen signals were detected. The X-BIS measurements were performed in a VG ESCA-LAB MK-II equipped with a preparation chamber. For X-BIS, the photonenergy of $h\upsilon = 1486.5$ eV was used and total resolution of about 0.75 eV was obtained. The samples were mechanically cleaned in the preparation chamber under UHV condition and then introduced into the spectrometer. The sample was cooled to liquid nitrogen temperature during measurements to prevent oxidation. No oxygen signals were detected during the course of the measurements.

In all experiments, the work functions of the spectrometers were carefully adjusted, referring to the spectra of evaporated gold or silver films. These adjustments are crucial for the present study, and we have paid special attention for their determinations.

III. RESULTS AND DISCUSSION

First let us summarize the results of the RPES study on UPd_2Al_3 since detailed discussions have not been given in previous papers.[3,6,7] Figure 1 shows the U 5f difference spectrum of UPd_2Al_3, obtained by a subtraction of the off-resonance spectrum ($h\upsilon = 101$ eV) from the on-resonance spectrum ($h\upsilon = 106$ eV). The spectrum is in agreement with the result of the previous experiment.[3] The U 5f spectra display a generic triangular shape having very large amplitude near E_F and tailing off slowly to high binding energies. The calculated U 5f DOS with a Gaussian broadening of 0.7 eV is superimposed for a comparison. Major differences between the calculated DOS and the experimental spectrum are as follows.

First, the position of the prominent feature near E_F is different in the experiment and the calculation. The E_F is found at the half-intensity point in the experimental spectrum, while it is located almost at the peak in the calculation. The placement of E_F at a half-intensity point is only strictly correct for a flat density of states cut off by a Fermi function
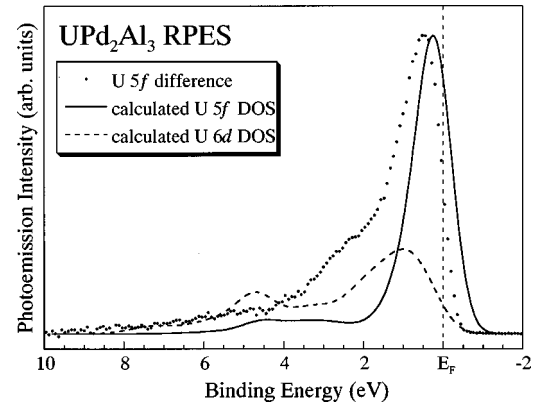

FIG. 1. The comparison of the U 5f difference spectrum with the calculated U 5f and U 6d DOS with the Gaussian broadening of $\Gamma_G = 0.7$ eV.

and broadened. This experimental spectrum is far from flat, and E_F is expected to be located at the peak if the large DOS exists at E_F, as seen in the calculations. The position of E_F in the experimental spectrum suggests that an actual intensity at E_F is lower than that of the calculated U 5f DOS.

Second, the experimental spectrum has a humped feature around 2.5 eV below E_F, which is not seen in the calculated U 5f DOS. It has been pointed out that the U 6d states are also enhanced by a procedure of the subtraction, and appeared around this energy region.[10] To consider the contribution from U 6d states, we have shown the calculated U 6d DOS in Fig. 1. The calculated U 6d DOS has broad structure, and has its maximum at about 1.0 eV below E_F. Hence, the U 5f difference spectrum cannot be reproduced by the calculated DOS, even if the contributions from the U 6d states are also considered. This is in contrast with the calculated Pd 4d DOS, where a good agreement was obtained for the off-resonance spectrum in shape and position.[3,6]

Next let us consider the RPES spectra of $U_xLa_{1-x}Pd_2Al_3$ for $x = 0.6$, 0.25, and 0.1 to understand the origin of the U 5f difference spectrum. Figure 2 shows U 5f difference spectra of $U_xLa_{1-x}Pd_2Al_3$, obtained by the subtraction of the off-resonance spectra ($h\upsilon = 101$ eV) from the on-resonance spectra ($h\upsilon = 106$ eV). The spectrum of UPd_2Al_3 ($x = 1.0$) is superimposed in each spectrum for comparison. The most remarkable point in these spectra is that their spectral features are not essentially influenced by the substitution of uranium atoms with lanthanum atoms. If the spectrum is originated with the U 5f band states, narrowing or shifting of the spectra with the substitutions should be expected. The absence of any changes in these spectra suggests that they are governed by the interaction between uranium and neighboring palladium and aluminum sites, with negligible contributions from neighboring uranium sites.

Accordingly, the above results indicate that the RPES spectrum of UPd_2Al_3 is governed by a single site effect of the uranium sites, and the band-structure calculation cannot be a good starting point for the description of the RPES spectrum. This result is inconsistent with the agreement between the experimental data and the results of the band-structure calculations in the dHvA experiments and the magnetic properties. Here, we consider the origins of these inconsistencies.
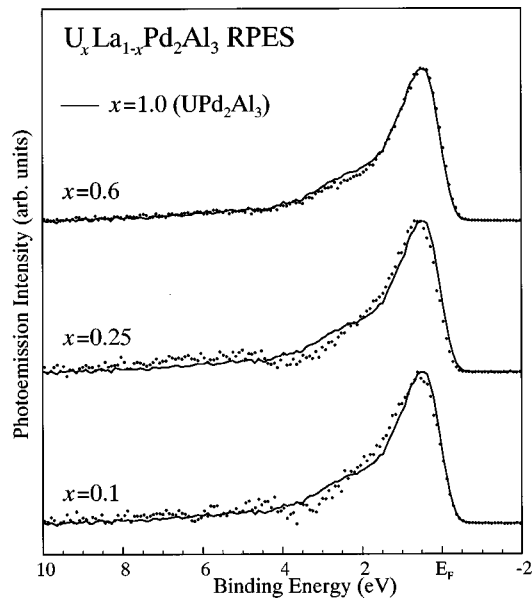
FIG. 2. The U 5*f* difference spectra of $U_xLa_{1-x}Pd_2Al_3$ for x = 0.1, 0.25, and 0.6. The spectrum of UPd_2Al_3 ($x = 1.0$) is superimposed in each spectrum for comparison.
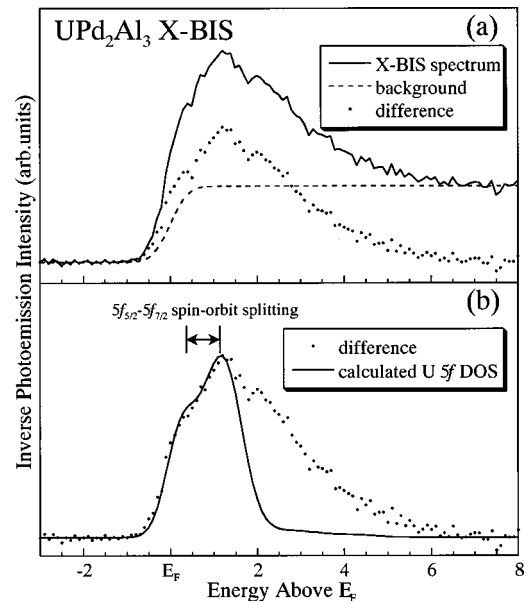

FIG. 3. (a) The X-BIS spectrum of UPd_2Al_3 and the procedure of the background subtraction. The dashed line shows structureless background to account for the transitions into non-5*f* states. The solid line indicates the result of the subtraction. (b) X-BIS U 5*f* spectrum of UPd_2Al_3, together with the calculated U 5*f* DOS with the Gaussian broadening of $\Gamma_G = 0.75$ eV.

One possible explanation is that the RPES process affects the U 5*f* band states, and the U 5*f* band states are not correctly imaged in the RPES spectrum. The RPES process is understood within an atomic process, first described by Fano.[11] The application of this scheme to the *f*-electron system has been investigate in many works.[12] However, a realistic treatment of this process is still a difficult issue, and it is still unclear whether this complicated process can correctly project the bandlike U 5*f* electrons also.

Another possible explanation is that the contributions from the sample surface dominate the RPES spectrum, and the localized nature of the U 5*f* states is observed. The escape depth of photoelectrons in the present measurements is considered to be about 5 Å, which corresponds to about two atomic layers. The lower coordination in the surface layers generally results in a narrowing of band states, and this may even result in a breakdown of their delocalization. This is actually in the case of some Ce-based compounds, where the different spectral features are observed in different excitation photon energies, i.e., different surface sensitivities.[13] For actinide materials, the theoretical calculations suggested that the U 5*f* electors are more localized in the surface than in the bulk.[14] Experimentally, Allen *et al.* have recently measured the valence-band spectra of UAl_2, using photon energy from 40.8 to 1486.5 eV.[15] However, they did not observe any significant changes in the spectral shape by changing the photon energy. This implies that the surface effects play a minor role in the photoemission spectra of UAl_2. Therefore, the importance of surface effects in the RPES spectrum of UPd_2Al_3 is still an open question.

To avoid the influences from the RPES process and the surface contributions, the photoemission experiments with higher photon energies, but not core electron excitation threshold, are required. We have previously measured the photoemission spectra of UPd_2Al_3 at $h\upsilon = 1486.5$ eV, where these contributions can be neglected.[16] However, in these spectra, the contributions from the Pd 4*d* states are predomi-

nant, and the contribution from the U 5*f* states were difficult to estimate. Meanwhile, the situation is much more preferable in the X-BIS measurements since there are no contributions from Pd 4*d* states in the unoccupied part. For this reason, we have measured the X-BIS spectrum of UPd_2Al_3 and compared it with the calculated U 5*f* DOS. The solid line in Fig. 3(a) shows the X-BIS spectrum of UPd_2Al_3. To account for the transitions into non-U 5*f* states, such as the U 6*d* states, a structureless background is assumed. This background shape is based on the BIS measurements of UPd_2Al_3 at $h\upsilon = 20$ eV, where the non-U 5*f* contributions dominate the spectrum.[17] The obtained difference spectrum, indicated by the dots in Fig. 3(a), can be considered as the contributions only from the U 5*f* states. Figure 3(b) show the comparison between the obtained U 5*f* difference spectrum and the calculated U 5*f* DOS with Gaussian broadening of 0.75 eV to account for the instrumental resolution. The spectrum is much broader than the calculated U 5*f* DOS; however, the structure near E_F is well matched with the calculation. In particular, a fine structure, originated with the $5f_{7/2}$-$5f_{5/2}$ spin-orbit splitting, is well reproduced by the calculation. The X-BIS studies on various uranium compounds showed that this structure is considerably different in different compounds.[18] This agreement may imply the applicability of the band-structure calculations to the U 5*f* states, although the experimental spectral width is broader than that of the calculation. This kind of broadening has been observed in the inverse-photoemission spectra of HF uranium compounds, and is understood due to the Coulomb interaction between U 5*f* electrons.[19] Recent angle-resolved photoemission studies on HF uranium compound UPt_3 also showed that U 5*f*–derived states have narrow-band behaviors.[20] This result shows the possibilities of proving the U 5*f* band states in

HF uranium compounds by the photoemission measurements.

sponsible for the absence of the U 5f band states in the RPES spectrum.

CONCLUSION

The obtained RPES spectrum of UPd$_2$Al$_3$ could not be reproduced by the calculated U 5f DOS, even when the comparison is limited to a near E_F part. Moreover, the spectra were insensitive to the substitution of uranium atoms by lanthanum atoms. These two facts suggest that the band-structure calculation cannot be a good starting point for the understanding of the RPES spectrum of UPd$_2$Al$_3$, even though the itinerant pictures of U 5f electrons are strongly supported in this compound. We propose that the contributions from the RPES process or the surface effects are re-

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