



Contents lists available at ScienceDirect

## Journal of Electron Spectroscopy and Related Phenomena

journal homepage: [www.elsevier.com/locate/elspec](http://www.elsevier.com/locate/elspec)



# Recent progress of soft X-ray photoelectron spectroscopy studies of uranium compounds

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### ARTICLE INFO

#### Article history:

Available online xxx

#### Keywords:

Photoelectron spectroscopy  
Uranium compounds  
Synchrotron radiations

### ABSTRACT

Recent progresses in the soft X-ray photoelectron spectroscopy (PES) studies ( $h\nu \gtrsim 100$  eV) for uranium compounds are briefly reviewed. The soft X-ray PES has enhanced sensitivities for the bulk U 5*f* electronic structure, which is essential to understand the unique physical properties of uranium compounds. In particular, the recent remarkable improvement in energy resolutions from an order of 1 eV to 100 meV made it possible to observe fine structures in U 5*f* density of states. Furthermore, soft X-ray ARPES becomes available due to the increase of photon flux at beamlines in third generation synchrotron radiation facilities. The technique made it possible to observe bulk band structures and Fermi surfaces of uranium compounds and therefore, the results can be directly compared with theoretical models such as band-structure calculations. The core-level spectra of uranium compounds show a systematic behavior depending on their electronic structures, suggesting that they can be utilized to determine basic physical parameters such as the U 5*f*-ligand hybridizations or Coulomb interaction between U 5*f* electrons. It is shown that soft X-ray PES provides unique opportunities to understand the electronic structures of uranium compounds.

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## 1. Introduction

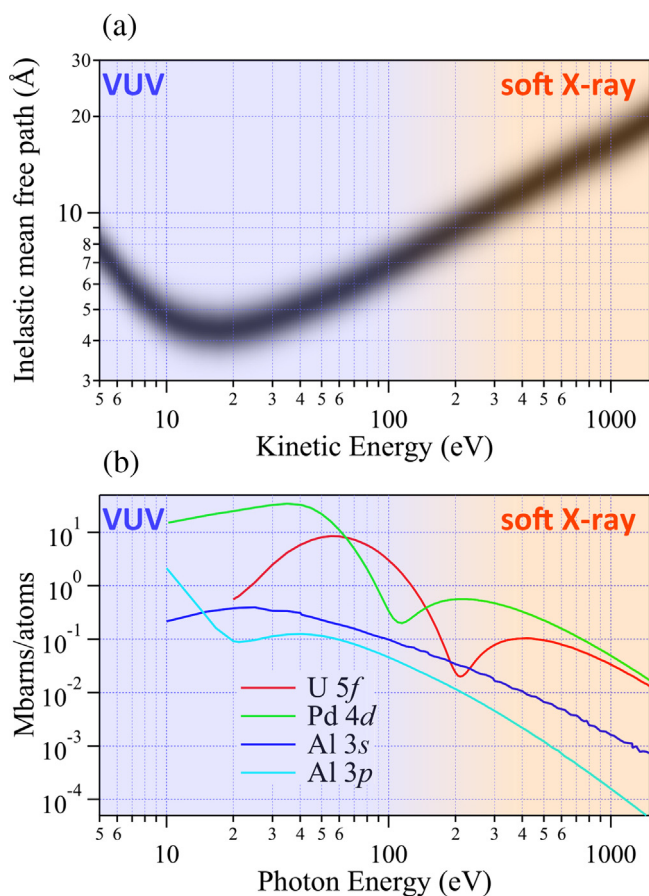
Actinide compounds show a rich variety of physical properties due to the localized and itinerant natures of actinide 5*f* electrons. In particular, the interplay between magnetisms and superconductivity is a key feature of those compounds. For example, most of actinide superconductors show the coexistence of superconductivity and some types of magnetic ordering, suggesting that the magnetic instabilities are playing an essential role in the superconductivity in actinide compounds [1].

Meanwhile, photoelectron spectroscopy (PES) is a very powerful experimental technique to study the electronic structures of materials. The technique has been applied to many strongly-correlated materials to reveal their electronic structures. PES has also been utilized for strongly correlated *f*-electron materials. On the other hand, actinide 5*f* materials are very difficult to measure by PES due to their radioactive natures. Only limited groups have been able to perform

PES experiments for uranium compounds. The studies of uranium compounds started in early 1980s by using laboratory light sources. In the middle of 1980s, synchrotron radiation-based PES experiments began to be commonly applied for uranium compounds by several groups. In those periods, most of studies measured the valence band spectra by using vacuum-ultraviolet (VUV) light ( $h\nu < 100$  eV). Meanwhile, there were also soft X-ray ( $h\nu \gtrsim 100$  eV) PES studies for uranium compounds from the early 1980s [2], and those studies became recognized as an important tool to understand the nature of U 5*f* electronic structures as discussed in the following sections.

In the present paper, we shall outline the recent progress of the soft X-ray PES studies for uranium-based compounds. The paper is structured as follows. Important aspects of soft X-ray PES are summarized in Section 2. The impact of the improvement in the energy resolution on the valence band spectra is demonstrated in Section 3. The development of soft-X-ray ARPES and its application to uranium compounds is discussed in Section 4. Challenges to understand the core-level spectra of uranium compounds are discussed in Section 5. Finally, the results are summarized,

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**Fig. 1.** (a) Inelastic mean free path of photoelectrons in solids [3] and (b) the photoionization cross-sections of U 5*f*, Pd 4*d*, Al 3*s*, and Al 3*p* orbitals [5].

and possible future directions of these studies are stated in Section 6.

## 2. Soft X-ray photoemission studies for *f*-materials

In this section, important aspects of soft X-ray PES are summarized. Fig. 1(a) shows the escape depth of photoelectrons as a function of their kinetic energy [3]. Since inter-band scatterings become dominant in the kinetic energy region of  $E_{\text{kin}} = 10 - 100$  eV, the curve has a minimum in this energy region. Since the lattice constants of materials are ranging from a few to 10 Å, PES experiments using photon energy less than  $h\nu < 100$  eV are dominated by signals from the first surface layer of materials. Therefore, it is very important to use high photon energies to avoid the strong contributions from surface layers. Experimentally, Sekiyama et al. [4] demonstrated the importance of the enhanced bulk sensitivities for *f*-electron materials.

Another important point is the photoionization cross-sections of 5*f* orbitals relative to those of *s*, *p*, and *d* orbitals of the other elements. Fig. 1(b) shows the photoionization cross-section of some atomic orbitals [5]. The photoionization cross-sections generally decrease as the photon energy increases. Meanwhile, each orbital has a considerably different dependence on the photon energy. For high photon energies, the cross-section of 5*f* orbital relative to those of *s*, *p*, and *d* orbitals increases. It becomes dominant in the photon energies of  $h\nu \gtrsim 500$  eV. Therefore, the soft X-ray PES has enhanced sensitivities for bulk 5*f* electronic structures.

Although an enhanced bulk sensitivity can also be achieved by very-low-energy photons ( $h\nu < 10$  eV), the relative photoionization cross-section of U 5*f* orbitals are much smaller than those of *s*, *p*,

and *d* states in these photon energies. In particular, contributions from *d* states are strongly enhanced in this photon energy region. Therefore, PES spectra measured by very-low-energy photons are generally dominated by the contributions from *s*, *p*, and *d* orbitals, and the contributions from U 5*f* states are difficult to observe.

In these 20 years, important progress has been made in the soft X-ray PES techniques thanks to the development of soft X-ray beamlines in third generation synchrotron radiation facilities [6–9]. The major progress are the improvement of energy resolutions and the development of the soft X-ray ARPES technique. The energy resolution of the soft X-ray PES has improved from the order of 1 eV to better than 0.1 eV. This makes it possible to observe fine structures in the PES spectra as it is shown in the next section. The increase of available photon fluxes in the soft X-ray beamlines as well as the development of the modern display-type photoelectron spectrometer significantly improved the efficiency of soft X-ray PES. These developments further made it possible to measure soft X-ray ARPES with energy resolutions of  $\Delta E \sim 100$  meV within a practical acquisition time as discussed in the next section.

In addition, the quality of samples and their sample cleaning methods have also been improved. The PES studies conducted until 1990s generally utilizes polycrystalline samples, and their clean sample surfaces have been prepared by scraping under ultra-high vacuum (UHV) conditions. However, it has been reported that the spectra from scraped surface are often different from those from cleaved surface of single crystals [10]. Generally, spectra obtained by cleaving give sharper spectra, and it was realized that scraping does not always work especially for strongly correlated materials.

## 3. Valence band spectra of uranium compounds

The valence band spectra of uranium compound are very important to reveal the itinerant versus localized natures of U 5*f* electrons. In particular, the key questions are the energy position of U 5*f* states and whether they have finite contributions to  $E_F$ . Valence band spectra of uranium based compounds have been measured using laboratory light sources such as Mg  $K\alpha$  ( $h\nu = 1253.6$  eV) or Al  $K\alpha$  ( $h\nu = 1486.5$  eV). However, the energy resolution was an order of 1 eV, and fine structures in the valence band spectra could not be resolved. Meanwhile, in the middle of 1980s, synchrotron radiations began to be applied to the photoemission experiments of uranium compounds. In particular, the huge enhancement in the cross-section of 5*f* orbitals due to the  $5d - 5f$  resonance ( $h\nu \sim 98$  eV) has been used to identify the contribution from U 5*f* states. There are a number of  $5d - 5f$  resonant photoemission spectroscopy (RPES) studies on uranium compounds [11]. In general, the U 5*f* spectra show a triangular line shape having a sharp peak in the vicinity of  $E_F$ . Meanwhile, the spectra do not show significant changes from compound to compound [12], and the origin of these spectral line shapes has been debated.

One point of view is that the spectra represent the itinerant U 5*f* states, having large contributions to  $E_F$ . In this scenario, the spectra can be understood by band-structure calculations based on the local density approximation (LDA). Another point of view is that the spectra represent the localized nature of U 5*f* states. In this case, the spectra can be understood by the impurity Anderson model which has been applied to the Ce-based compounds.

To solve this localized versus itinerant problem, La or Y-diluted alloys are good target materials to understand the lattice effect of U 5*f* electrons. Sarma et al. studied the  $5d - 5f$  RPES spectra of  $(U_xY_{1-x})B_4$ , and suggested that U 5*f* electrons have essentially itinerant character, suggesting that the spectral line shape can be understood by band-structure calculation [13]. Meanwhile, Kang et al. measured the  $5d - 5f$  RPES spectra of  $(U_xY_{1-x})Al_2$ , and suggested that the single site effect is dominant in the valence band

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