

Observation of the surface $4f$ state of CePd_7 by means of the resonant-inverse-photoemission study at the Ce $4d$ absorption edge

K. Kanai, Y. Tezuka, M. Fujisawa, Y. Harada, and S. Shin

Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Tanashi, Tokyo 188, Japan

G. Schmerber, J. P. Kappler, and J. C. Parlebas

IPCMS-GEMME (UMR 46 CNR), Université Louis Pasteur, 23, rue du Loess, 67037 Strasbourg, France

A. Kotani

Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

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The resonant inverse photoemission study (RIPES) of CePd_7 , has been carried out at the Ce $4d \rightarrow 4f$ absorption edge. The strong resonant enhancement of the $4f$ cross section enables us to distinguish two $4f$ components in the empty electronic state near the Fermi level. The incidence-angle dependence of the RIPES indicates a clear difference between ground-state configurations at the bulk and surface. It is found that the former shows a strongly hybridized $4f$ state, while the latter shows a localized $4f$ character. The angle dependence of the RIPES of α -Ce metal has been also carried out and similar results as those of CePd_7 were obtained. The RIPES at the Ce $4d \rightarrow 4f$ edge is found to be a powerful method to investigate the surface $4f$ state. [S0163-1829(97)07604-2]

I. INTRODUCTION

It is known that Ce compounds show interesting electronic properties that are mainly caused by the partially localized character of the $4f$ electron. The high-energy spectroscopy has played an important role in the investigation of the electronic structure of these strongly correlated systems. Furthermore, an analysis of these measurements has achieved a great success within the framework of the degenerate impurity Anderson model (IAM).¹

Some Ce compounds form the so-called valence fluctuation (VF) system, where the $4f$ electron has an itinerant character because of the strong hybridization with the conduction band. For typical VF systems, lower values of the Sommerfeld coefficient γ and the Pauli-like susceptibility χ_0 were reported.² The $4f$ occupancies in the ground state of typical VF systems were shown to be about 0.8 by $3d$ x-ray photoemission spectroscopy (XPS), x-ray absorption spectroscopy (XAS), photoemission spectroscopy (PES), and bremsstrahlung isochromat spectroscopy (BIS) measurements.³ Also the valence extracted from the XAS measurement at Ce $2p$ ($L_{2,3}$) edge was usually found below 3.3.⁴ That is to say, the high-energy spectroscopy indicates that the ground state is mainly composed of $4f^1$ configuration even in VF systems.

On one hand, CePd_7 , has the lowest values of γ ($9.8 \text{ mJ K}^{-2} \text{ mol}^{-1}$) (Ref. 4) and χ_0 ($0.125 \times 10^{-3} \text{ emu mol}^{-1}$) [Ref. 5(a)] as compared to typical VF systems. Furthermore, the smaller ratio χ_0/γ ($0.012 \text{ K}^2 \text{ J}^{-1}$) [Ref. 5(b)] is comparable with the case of nearly-free-electron systems. Moreover the valence number was determined to be 3.5 by XAS measurement at the L_3 edge.⁵ These facts suggest that CePd_7 is considered to belong to the strong hybridization limit: a very high Kondo temperature T_K which is a characteristic constant of the system, is expected. On the other hand, the com-

plicated structure of Ce- $3d$ XPS spectra suggests the strongly correlated nature of the electronic structure of CePd_7 .⁶

The crystal structure of CePd_7 has been confirmed to be an α -Pd fcc structure with a lattice parameter of 4.002 \AA . The Ce ion is surrounded by 12 nearest-neighbor Pd atoms.⁷ The direct f - f overlapping is negligibly small owing to a large Ce-Ce spacing ($\sim 5.67 \text{ \AA}$), and so, the $4f$ electron of CePd_7 might migrate mainly through the hybridization between Ce $4f$ and Pd valence states. Therefore, we can treat an $4f$ electron on one Ce site as almost isolated, and so IAM is adequate to describe approximately the electronic structure of CePd_7 .

The $4f$ -electronic structure at the outermost surface layers of the intermetallic Ce compounds is often different from that of bulk due to different hybridization strengths. Generally, the surface $4f$ state of the Ce compound is γ like. Recent analysis of the $2p$ XAS and $3d$ XPS spectra by Iwamoto *et al.*⁸ reported that the occupancy of Ce $4f$ state at the surface and bulk of CePd_7 is 0.94 and 0.57, respectively. In marked contrast to the bulk $4f$ electron, the surface's $4f$ electron is well localized. This manifest difference of $4f$ -electronic structures may be reflected in the inverse photoemission spectroscopy (IPES) spectrum.

The IPES is known to be a useful measurement to investigate the unoccupied states. However, its cross section is much smaller than in the corresponding photoemission process. Moreover, the small magnitude of the $4f$ cross section prevents us from distinguishing the $4f$ signal from the non- f (for example, Ce $5d$) signals and the large background in the IPES spectrum.⁹ Recently, several resonant IPES (RIPES) measurements of Ce compounds near the Ce $3d$ (M_5) absorption edge around 883 eV have been performed.^{10,11} They have demonstrated the great ability of the RIPES measurement to enhance the magnitude of only the $4f$ signal due to

the resonance effect. Therefore, the RIPES is known to be a powerful tool to investigate $4f$ -electron systems.

In this paper, the RIPES measurement has been performed near the Ce $4d$ ($N_{4,5}$) absorption edge of CePd₇. Two sharp peaks are resonantly enhanced near the Fermi level. These peaks show different excitation energy dependencies. Furthermore, the angle dependence of RIPES can resolve these components into bulk and surface states, because of its surface sensitivity.

II. EXPERIMENT

The sample preparation and characterization have been presented elsewhere.^{5,6} Measurements were performed in an ultrahigh vacuum chamber where the base pressure is about 7×10^{-11} Torr. The CePd₇ sample was cleaned at liquid-N₂ temperature by scraping with a diamond file in a vacuum every 30 min. The Ce metal was evaporated to the molybdenum plate at 30 K. The surface cleanliness was checked by monitoring that there is no O 1s x-ray emission signal.

A filament-cathode-type electron gun was used for the excitation source. The kinetic energy (E_k) of the electron was calibrated by the electron energy analyzer. The IPES was measured by the soft x-ray emission spectrometer of the Institute for Solid State Physics,¹² which covers the wide photon energy range from 15 to 1200 eV. The spectrometer uses the Rowland circle geometry that consists of gratings with groove density of 300, 1200, 2400 lines/mm and the Cs-coated multichannel detector. We used a 300-lines/mm grating in this measurement. The Fermi-level position was determined by referring to the Fermi edge in the IPES spectra of Au which was evaporated on the same sample holder. The resolution of this system is 1.0 eV at $E_k=124$ eV.

III. RESULTS AND DISCUSSION

Figure 1 shows the excitation energy dependence of the IPES spectra of CePd₇ for the incident electron energy in the Ce $4d \rightarrow 4f$ region. The abscissa is the energy above the Fermi level that was calibrated by the Fermi edge of gold. The broad bands indicated by the vertical bars are the normal Ce $4d$ fluorescence that is caused by the Ce $4d$ core hole created by the electron excitation. The vertical bars located at higher energy show the fluorescence bands caused by the Ce $5p \rightarrow 4d$ transition. It is found that two separate resonances near the Fermi level show conspicuous enhancement around $E_k=124$ eV. Obviously a peak at the lower-energy side, which we name the f^1 state, mainly originates from the $4f^0$ configuration in the ground state and the other, named the f^2 state, originates from the $4f^1$ configuration. The energy separation between the f^1 peak and the Fermi level is about 0.95 eV, which reflects extremely high Kondo temperature (about 1×10^4 K). The extremely high T_K of CePd₇ reflects the very strong hybridization between the $4f$ state and the conduction band. This result is consistent with the strong hybridization picture of the CePd₇ system, which is expected by the small values of the γ and χ_0 .

The normal IPES process is represented for the transition to Ce $4f$ states as follows:

$$|4d^{10}4f^n\rangle + e^- \rightarrow |4d^{10}4f^{n+1}\rangle + h\nu. \quad (1)$$

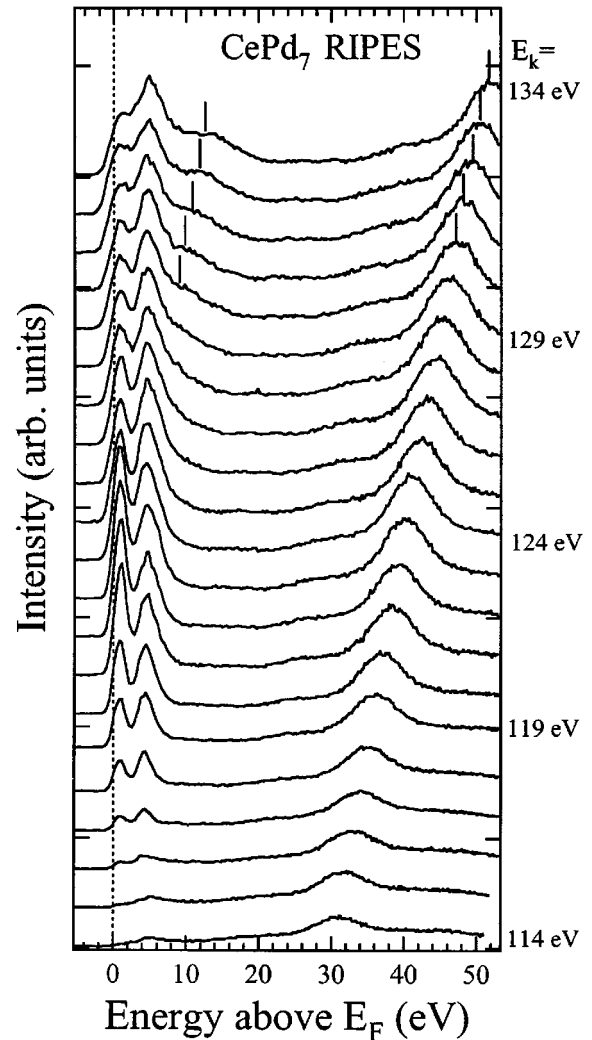


FIG. 1. The IPES spectra of CePd₇, near the Ce $4d \rightarrow 4f$ edge measured at liquid-N₂ temperature. The vertical dotted line shows the Fermi level. The abscissa is the energy above Fermi level (E_F). The numbers written on the side of the right axis represent the kinetic energy (E_k) of the electron.

Here, n is the configuration number of the $4f$ electrons in the ground state. For the incident energy range of the present experiment, the contribution from non- f conduction bands also coexists with the $4f$ contribution in the normal IPES. In the RIPES experiment, on the other hand, the resonant processes are expressed by the following processes:

$$|4d^{10}4f^n\rangle + e^- \rightarrow |4d^9 4f^{n+2}\rangle \rightarrow |4d^{10}4f^{n+1}\rangle + h\nu. \quad (2)$$

Since the initial and final states are the same in these two processes (1) and (2), they interfere with each other. Therefore, the $4f$ cross section increases when the excitation energy is tuned to Ce $4d \rightarrow 4f$ absorption edge and we can extract the Ce $4f$ contribution.

Figure 2 shows the comparison between the spectrum measured at $E_k=114$ eV and that at 126 eV. Their spectral intensities are normalized at the f^2 peak intensities. The electron energy $E_k=114$ eV is just below the giant resonance of the Ce $4d \rightarrow 4f$ absorption. The line shapes of the f^2 peaks apparently are different from each other. At 114 eV, the f^2 peak has a wider and asymmetric line shape as compared

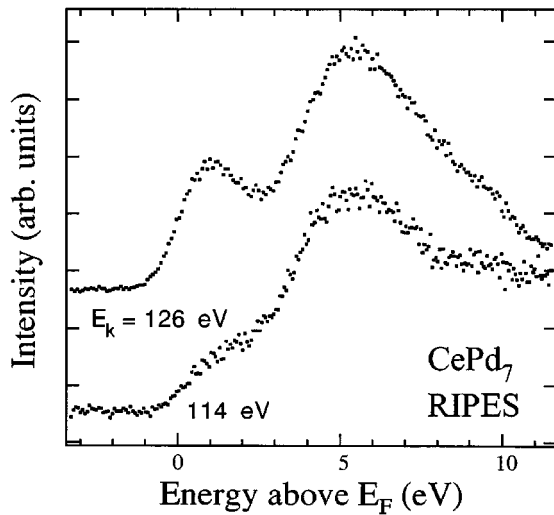


FIG. 2. Comparison between the IPES spectra near E_F measured at $E_k=114$ and 126 eV.

with that of 126 eV. As a possibility of the change of the line shape, it may reflect the band structure except the $4f$ component in CePd_7 , because the cross section of the $4f$ component is less below the resonance energy. In fact, the band-calculation curve⁶ well reproduces the line shape, if the energy position of the calculation is shifted to the higher energy by 1.4 eV. As another possibility, one can consider the change of line shape may reflect the selection rule on the resonance of the f^2 state, since the $\text{Ce } 4d \rightarrow 4f$ absorption has several fine structures in the energy region below the giant resonance so that the f^2 state causes the weak enhancement just below the giant resonance. In fact, the $\text{Ce } 5p \rightarrow 4d$ fluorescence is observed at $E_k=114$ eV, since the $\text{Ce } 4d \rightarrow 4f$ excitation has already occurred at this energy. Tanaka and Jo¹³ have pointed out that the weakly enhanced f^2 state just before the giant resonance has a wider line shape with several multiplet structures than that of the most enhanced one.

Figure 3 shows the excitation energy dependencies of the intensity of the f^1 and f^2 peaks. These curves are obtained by plotting the intensities of the f^1 and f^2 peaks against the kinetic energy of the electron, which corresponds to the constant final-state spectra. Each line shows the different energy dependence. The peak energy of the f^1 curve is located at 124 eV and that of the f^2 curve at 124 – 129 eV, and both have broad and asymmetric line shape. The line shape in Fig. 3 is completely different from the constant final-state spectra of the RIPES at the $\text{Ce } 3d$ edges that were already measured for several Ce compounds.^{10,11,13} This fact indicates much larger electronic interactions between the $4f^n$ and $4d$ -core hole than those between the $4f^n$ and $3d$ -core hole. Here one should remember that the $4d$ absorption spectrum has much wider and asymmetric line shape than that of the $3d$ absorption spectra in metallic Ce .⁴ In Ref. 13, it is pointed out that the line shapes of these curves in Fig. 3 are strongly influenced by the magnitude of the $4f$ -ligand hopping integral in the intermediate state at the resonance, taking account of the multiplet structures and the selection rule on resonance. Further discussion and full analysis of the energy dependence of RIPES spectra will be made in a separate paper.

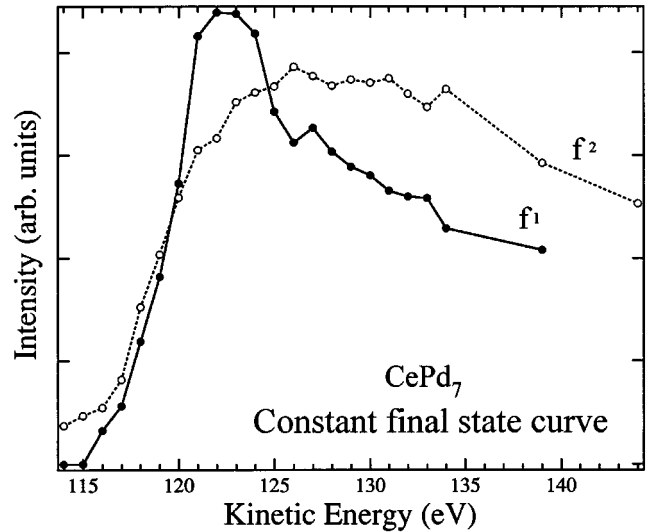


FIG. 3. The intensities of f^1 and f^2 peaks plotted against the kinetic energy of the electron.

The intensity ratio of the f^1/f^2 peak in the $\text{Ce } 4d$ RIPES spectrum of CePd_7 is much smaller than that of the $\text{Ce } 3d$ RIPES result of CeRh_3 , one of the most hybridized systems, as reported by Grioni *et al.*¹¹ Here, one can find that the intensity ratio of the f^1/f^2 peak on the resonance is unexpectedly small, supposing both states are identified with the bulk contribution.

It is said that the surface valence of rare-earth compounds is often lower than that of the bulk. In fact, it has been pointed out⁸ that the surface state shows a weak hybridization with a γ -like character in the analysis of $2p$ -XAS and $3d$ -XPS spectra of CePd_7 while the α -like bulk state shows a strong hybridization. The mean free path of the electron, the kinetic energy that is around 100 eV, is about 5 \AA ,¹⁴ so that the surface contribution strongly appears in the $4d$ RIPES spectrum. The angle dependence of the IPES spectra is useful to sort out both components. Higher sensitivity to surface is obtained by grazing incidence. Figure 4(a) shows the incidence-angle dependence of the RIPES measured at $E_k=124$ eV from 0° to 80° . The angle dependence was also measured at 118 eV, which is very similar to that in Fig. 4(a). It is clear that the intensity ratio of the f^1 and f^2 peaks increases by decreasing angles with decreasing sensitivity to the surface.

Iwamoto *et al.* calculated the BIS spectra of CePd_7 , where both the bulk and surface contributions are calculated independently and superposed with various weights.⁸ Figure 4(b) shows their results, where the relative intensity of the surface contribution is changed as a parameter. Though their calculation was limited to the off-resonance case, they took into account only the $4f$ contribution, so that their result should be compared with the experimental data of RIPES that reflects the $4f$ contribution. The f^1 state of the calculated BIS spectrum at 0% surface contribution is in good agreement with our experimental spectrum. The angle dependence in Fig. 4(a) agrees well with that of the calculation of BIS spectra by Iwamoto *et al.*⁸ The linewidth of the f^1 state is much wider in the experiment than in the calculation. A slight shoulder seems to be found at the Fermi edge for the

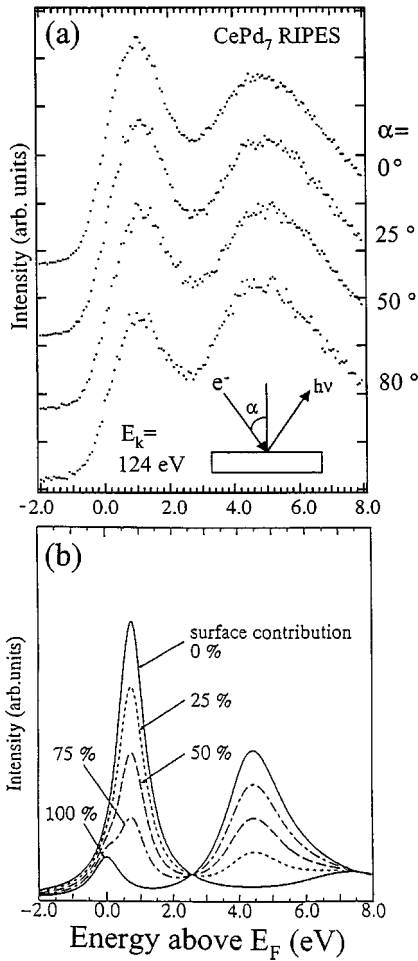


FIG. 4. (a) The angle dependence of the on-resonant RIPES spectra of CePd_7 measured at $E_k = 124$ eV. (b) The calculation (Ref. 8) of the BIS spectra of CePd_7 where the surface contribution changes from 0% to 100%.

spectrum at the 80° incidence angle. The predicted doublet structures of the f^1 state at 75% surface contribution are not clearly resolved in the experiment because of its wide line-width. The surface contributions in the experimental spectra from 0° to 80° correspond to be in the range from 50% to 75% in the calculations.

The surface contribution in the RIPES spectrum has been calculated by the following simple formula:¹⁵

$$I_s / (I_s + I_b) = 1 - \exp(-a/l \cos \alpha), \quad (3)$$

where I_s and I_b are the surface and the bulk state intensities, respectively, l is the mean free path of the electron, α is the incidence angle, and a is the thickness of surface layer. Here, l is assumed to be 5 \AA for the electron with the kinetic energy of about 100 eV and a is assumed to be 2 \AA , which corresponds to the surface monolayer of CePd_7 . Figure 5 shows the surface contribution of Ce $4d$ and Ce $3d$ edges in the spectra against the incidence angle. The incidence angle from 0° to 80° correspond to the surface contribution from 40% to 90% in Fig. 5. It is in very good agreement with a rough estimation of the surface contribution from 50% to

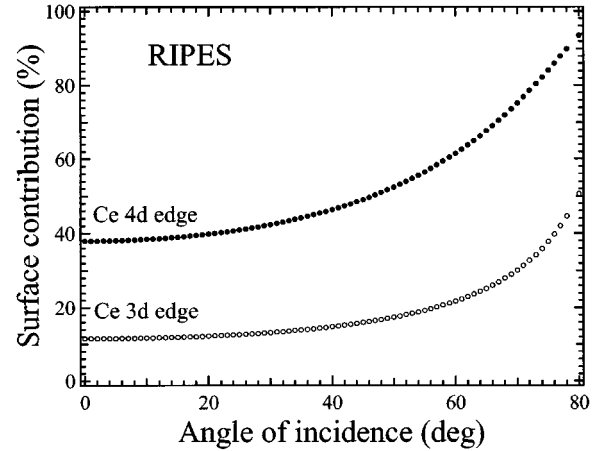


FIG. 5. The angle dependence of the surface contributions in the Ce $4d$ and $3d$ RIPES spectra.

75%, which is obtained by the comparison between the calculated and the experimental line shapes between the f^1 and f^2 states, as shown in Fig. 4.

It is adequate to consider that the f^1 and f^2 peaks are composed of the bulk and the surface contribution, respectively. Therefore, it is concluded that the high T_K extracted from the f^1 peak position represents the extremely strong hybridization of the bulk $4f$ state and the f^2 peak comes from the surface $4f$ state. The different dependence on the excitation energy of the f^1 and f^2 peaks indicates the very contrastive electronic structure; that is, the bulk is α -Ce-like and the surface is γ -Ce-like. For more detailed discussions on the RIPES spectra (e.g., the incident energy dependence), the calculation of the RIPES will be made in the near future taking into account processes (1) and (2).

As another example of the angle dependence of the RIPES, Fig. 6 shows the angle dependence of the on-resonance spectra of α -Ce metal. The intensity of the f^1 state

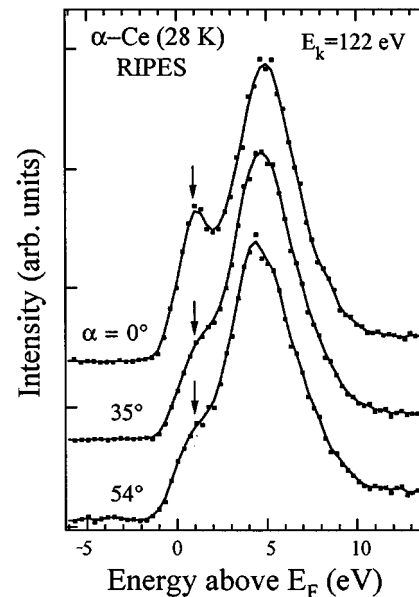


FIG. 6. The angle dependence of the on-resonant RIPES spectra of α -Ce metal.

indicated by arrows increases from grazing to normal incidence angle, while the f^2 state remains constant for each angle. Since there is a similar angle dependence of the spectra as in the case of CePd₇, it is found that the γ -like surface state also exists in the α -Ce metal. It may not be particular that the more localized state exists at the surface state of the Ce compounds. The RIPES is a powerful experimental method to study such $4f$ states.

Figure 5 shows the comparison of the angle-dependent surface contribution between the $4d$ and $3d$ RIPES. The Ce $4d$ RIPES is more surface sensitive than $3d$ RIPES, because of its short electron mean free path. Its angle dependence is also larger, so that it may be more powerful experimental method to measure the surface contribution in the $4d$ RIPES than in the $3d$ RIPES.

IV. CONCLUSION

In conclusion, the RIPES measurement near the Ce $4d$ absorption edge reveals the remarkable contrastive electronic structure at the bulk and surface state of CePd₇. The RIPES

at the Ce $4d \rightarrow 4f$ edge is found to be a powerful method to investigate the surface $4f$ state. The bulk is α -like and the surface is γ -like. The difference of the ground-state configuration at the bulk and surface reflects the separate resonances. The extremely high Kondo temperature ($kT_K \sim 0.95$ eV) of the bulk expresses the very strong hybridization between the $4f$ and ligand states. Our results are consistent with the previous calculation,⁸ though more detailed calculations will be needed. Due to the large Ce-Ce spacing, the calculation within the framework of the IAM seems to give a good agreement. The resonant enhancement of the $4f$ cross section makes it possible to distinguish between the specific contributions in the spectra near Fermi level. It is pointed out that the RIPES measurement around Ce $4d$ edge has a high sensitivity to the surface.

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