Resonant inverse photoemission spectroscopy at the prethreshold of the Ce-$N_{4,5}$ absorption edge in $CePd_3$

K. Kanai
RIKEN, Sayo-gun, Hyogo 679-5148, Japan

T. Terashima and A. Kotani
Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

T. Uozumi
College of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan

G. Schmerber, J. P. Kappler, and J. C. Parlebas
IPCMS-GEMM (UMR 7504 CNRS), University Louis Pasteur, 23, rue du Loess, 67037 Strasbourg, France

S. Shin
Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan and RIKEN, Sayo-gun, Hyogo 679-5148, Japan

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We performed the resonant inverse photoemission (RIPE) study on $CePd_3$ at the prethreshold region of the Ce-$N_{4,5}$ absorption edge. The surface effects on RIPE spectra are discussed through the investigation of the resonance behaviors. Comparison between the RIPE spectra and the calculated resonant-excitation probability of the intermediate states indicates the existence of specific excitation energy range, where a strong resonant enhancement occurs for the bulk or the surface $4f$ spectrum.

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Many Ce compounds are particularly attractive because they provide opportunities to challenge fundamental problems in solid-state physics such as electron correlations. Modern electron spectroscopies have played an important role in the studies of these systems. Photoemission (PE) and inverse PE (IPE) spectra directly probe the electronic structure around the Fermi level E_F. On the other hand, the structure in Ce $3d$ x-ray-photoemission spectra is sensitive to the initial $4f$ configuration state.[1] They show the fact that the many-body effect strongly affects the spectra. Moreover, the theoretical approaches within the framework of an impurity Anderson model (IAM) to these experimental results have been successful to estimate the parameters of the $4f$ electron systems.[2] However, we should pay attention to the surface contributions in the spectra because the probing depth of these measurements is less than 20 Å. The escape or penetration depth of the electron is equivalent to the length of several layers. Most of the phenomena of photoemission and inverse-photoemission occur in the surface region. Therefore, the role of surface effect is expected to be crucial for a correct interpretation of the spectra, to a varying extent.

Resonant IPE (RIPE) spectroscopy is a technique to investigate the electronic structure of a given material above E_F.[3,4] The unoccupied $4f$ electronic states below the vacuum level is known to be important to understand many interesting physical properties of Ce compounds. The RIPE process gives great enhancements of the $4f$ contributions to the IPE spectrum by the quantum-mechanical interference effects between a normal and a resonant IPE process.[5] We can obtain direct information from RIPE spectra about the unoccupied $4f$ states. On the other hand, in spite of its usefulness, RIPE measurement is a surface-sensitive technique, as are other spectroscopies. Especially, the RIPE spectrum at the $N_{4,5}$ edge has a great deal of surface contribution due to the shorter penetration depth of the incident electron. It is troublesome to pick up the bulk contribution in the spectra without the help of calculation because it strongly mixes with the surface contribution.

In this paper, we discuss surface effects on RIPE spectra by comparing the experimental results to the calculated ones. We exhibit the relationship between the bulk or surface sensitivity and the excitation energy that is specific to the RIPE spectra at the prethreshold of the $N_{4,5}$ edge. This clearly shows the ability of our measurement to take bulk- or surface-sensitive spectra.

Measurements are performed in an ultrahigh vacuum chamber where the pressure is about 5×10^{-11} Torr under the operation of an electron gun. Samples are kept around 20 K by closed-cycle ^{4}He refrigerator. Clean sample surface of polycrystalline $CePd_3$ sample is obtained by scraping the surface with a diamond file in an ultrahigh vacuum every $\sim$60 min at 20 K. The IPE spectra are measured by the soft x-ray-emission system that has a Rowland mounted-type spectrometer.[6] The E_F position is determined by referring to the Fermi edge in the IPE spectra of Au that is evaporated on the sample holder. In this work, the RIPE spectra are analyzed by means of an IAM with the full-multiplet coupling effect in a Ce ion. The details of the calculation were presented elsewhere.[4]

Figure 1(a) shows RIPE spectra of $CePd_3$ measured below the Ce-$N_{4,5}$ absorption edge that is situated around 120 eV.[7] The excitation energies E_{ex} are given at the left side of the

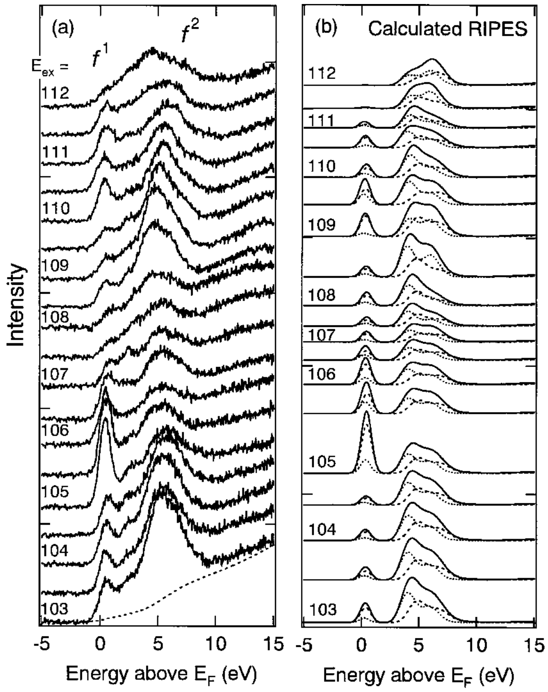

FIG. 1. (a) The experimental RIPE spectra and (b) the calculated RIPE spectra at the $N_{4,5}$ prethreshold of $CePd_3$. The numbers beside the left axes stand for the excitation energy E_{ex}. The broken and the dotted lines stand for the bulk and the surface spectra, respectively. The calculated spectra are broadened with a Gaussian function of width 0.5 eV half-width at half maximum (HWHM) in order to include the overall resolution and a Lorentzian function with the energy dependent lifetime width $\Gamma = 0.5 + 0.01|E - E_F|^2$ eV.

spectra. E_{ex} are distributed in the prethreshold region of the $N_{4,5}$ edge. The peak just above E_F is the so-called f^1 peak and the broad band at around 5 eV is the f^2 peak. The f^n peak $(n=1,2)$ is almost caused by the $4f^{n-1}\underline{c}^{n-1} \rightarrow \underline{4d}4f^{n+1}\underline{c}^{n-1} \rightarrow 4f^n\underline{c}^{n-1}$ RIPE processes, that is to say, the $4f^n$ peak reflects the weight of the $4f^{n-1}$ state in the initial state, where $n=1$, 2 and $\underline{4d}$ and $\underline{c}$ are the hole in the $4d$-core level and conduction band, respectively. It should be noted that the resonance process is a second-order optical process, which is caused by the excitation to the intermediate state $\underline{4d}4f^{n+1}\underline{c}^{n-1}$. Marked excitation energy dependence of the *f* peaks is clearly observed in Fig. 1(a). It is pointed out that the resonance behavior at the prethreshold (prethreshold resonance) is dissimilar to one above the threshold (giant resonance).[4] The resonance enhancement of the *f* peaks at the prethreshold occurs twice in a narrower range of E_{ex} at about $E_{ex} = 105$ and 110 eV. In Fig. 2 constant final-state spectra (CFS) of the f^1 peak are shown, which are measured below and above the threshold.[3] The CFS explicitly show the difference in the resonance behavior between the prethreshold and giant resonance. The CFS of the giant resonance, which has an asymmetric broad line shape, is reminiscent of the giant-absorption band in the $4d$-absorption spectra.[8] On the other hand, the CFS of the prethreshold resonance has a sharp form that is similar to the absorption spectra below the threshold. The sharpness of the prethreshold resonances is due to the relatively stable intermediate states in contrast to the giant resonance.

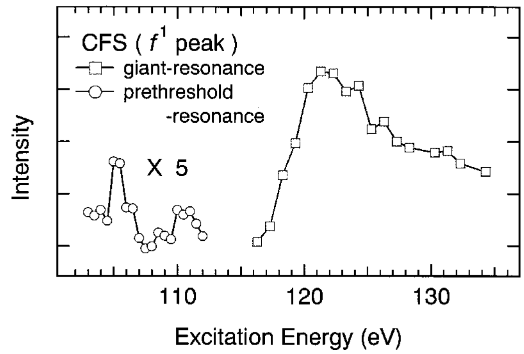

FIG. 2. CFS of the giant and prethreshold resonance. The spectra are obtained by plotting the integrated intensities of the *f* peaks against the E_{ex}.

The line shapes of the f^n peaks change with E_{ex} in Fig. 1(a). It seems to be natural to attribute the changes of the f^2 peak line shapes to the multiplet splitting $(^3H, ^1G)$ of the $4f^2\underline{c}$ final states. As a consequence of the strong exchange coupling between $4d$ and $4f$ spin, the intermediate state of f^2 peak with the configuration $\underline{4d}4f^3\underline{c}$ splits into many multiplets that spread out over 10 eV. Each of them is resonantly excited at different E_{ex}. Accordingly, the f^2 peak resonance has a strong dependence on E_{ex}. On the other hand, the f^1 peak is found to be intensely enhanced around $E_{ex} = 105$ eV and a weaker enhancement is observed at higher $E_{ex} \sim 110$ eV. The calculated RIPE spectra in the Ce-$N_{4,5}$ prethreshold are shown in Fig. 1(b). Superposing these bulk and surface spectra with a ratio of 1:1 makes up a total spectrum (full line). The parameter set for the calculation is listed in Table I. We derived the bulk and surface parameters from the analysis of the spectra ($3d$-XPS, X-BIS, $M_{4,5}$-RIPE and $N_{4,5}$-RIPE spectra) which possess various bulk sensitivity. ϵ_f, U_{ff}, and V are the $4f$ level, Coulomb potential between the $4f$ electrons and the hybridizaion strength between $4f$ and conduction electron states, respectively. U_{fc} represents the attractive potential between the $4f$ electron and $4d$ core hole. It is shown that the calculated RIPE spectra reproduce the observed ones in Fig. 1(a) at almost the whole prethreshold region, especially the strong enhancement of the f^1 peak in RIPE spectra at 105 eV, as well as the complicated resonant behavior of ^3H and ^1G multiplets in the f^2 peak.

In order to investigate the multiplet structure in the intermediate states of the RIPE process, we calculated the resonant-excitation probability of the intermediate states, $P(E_{ex})$, and show the results in Fig. 3. Figure 3(a) shows the calculated total $P(E_{ex})$. The $P(E_{ex})$ stands for the absorption intensities by $4d\epsilon l$-$4d4d$ Coulomb scattering, $4f^n\underline{c}^n\epsilon l$

TABLE I. The parameter sets for $CePd_3$ and the calculated average $4f$-number n_f. U_{ff} (=6.4 eV) and U_{fc} (=9.5 eV) are the same values for both the bulk and surface.

	ϵ_f (eV)	V (eV)	n_f
Bulk	−1.8	0.36	0.92
Surface	−2.3	0.28	1.0

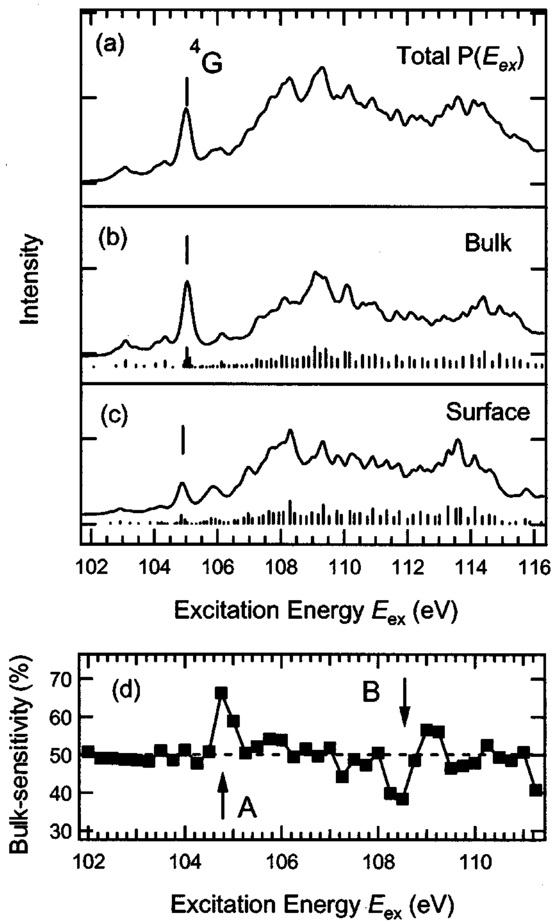

FIG. 3. The calculated $P(E_{ex})$ at the prethreshold region of $CePd_3$. (a) Total spectrum that is obtained by superposing the bulk and the surface spectra with the ratio of 1:1. (b) and (c) are bulk and surface spectra, respectively. The calculated spectra are broadened with a Lorentzian function of width 0.15 eV (HWHM). (d) The calculated bulk-sensitivity $I(\mathrm{Bulk})/I(\mathrm{Total})$ as a function of E_{ex} where $I(\mathrm{Bulk})$ and $I(\mathrm{Total})$ stand for the integrated intensities of the calculated bulk- and bulk+surface spectra in Fig. 1(b).

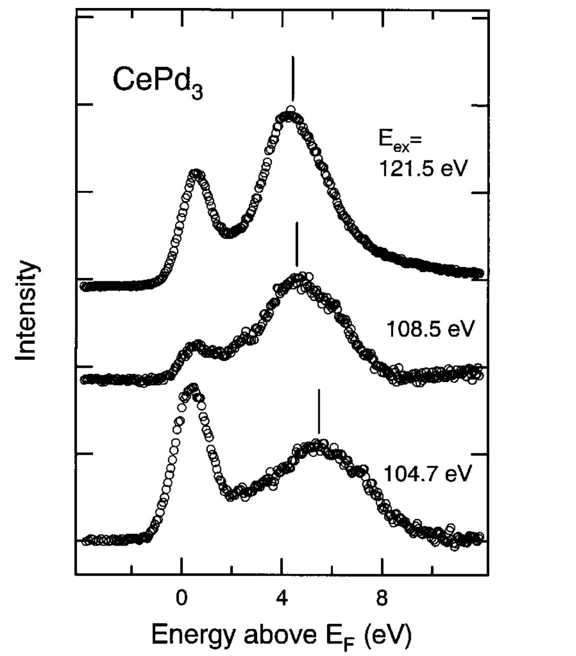

FIG. 4. The experimental RIPE spectra of $CePd_3$ that are measured at 104.7, 108.5, and 121.5 eV. The background is subtracted from the spectra. The vertical bars represent the energy position of the f^2 peaks.

$\rightarrow \underline{4d}4f^{n+2}\underline{c}^n$, $(n=0,\,1)$.[9] Here the ϵl is the incoming electron with angular momentum l with energy E_{ex}. Those transitions are the excitation processes into the intermediate states in the RIPE of the f^1 and f^2 peaks. Roughly speaking, $P(E_{ex})$ intensity accounts for a resonance enhancement of the RIPE spectrum. It is found that the strong absorption intensity at $E_{ex}=105$ eV in the $P(E_{ex})$ is mainly concerned with the ^4G multiplet in the $\underline{4d}4f^2$ final state. From a straightforward comparison with the RIPE spectra in Fig. 1(a) the intense peak of the $P(E_{ex})$ ^4G explains the dramatic enhancement of the f^1 peak in the RIPE spectra around $E_{ex}=105$ eV. In addition, the weaker resonance of the f^1 peak around 110 eV corresponds to the structures located between 108 and 111 eV in the $P(E_{ex})$. The ^4G final state of the $P(E_{ex})$, which is excited by the scattering between the $\epsilon g(l=4)$ and $4d$-core electrons, radiatively decays into the ^2F final states of the RIPE process. The $^4G \rightarrow {}^2F$ transition becomes weakly dipole allowed due to an admixture of ^2G states through a spin-orbit interaction. In the giant-resonance region, ^2S,^2D,^2G,^2I, and ^2L intermediate states are excited through the $4d\epsilon l$-$4f4f$ Coulomb scattering. With a restriction by the dipole selection rule, ^2D and ^2G intermediate states give rise to dramatic resonance enhancements of the f^1 peak. These states mix with the quartet states, ^4P,^4D,^4F,^4G,^4H, and ^4I, so they have weak weight in the prethreshold region.

Hereafter, we focus our discussion on the interesting connection between the above resonance effects on the f^1 peak and bulk sensitivity of the RIPE spectrum. The calculated $P(E_{ex})$ for the bulk and the surface are shown in the Figs. 3(b) and 3(c), respectively. It should be noted that the sharp peak ^4G in the bulk spectrum is much larger than that in the surface spectrum. Because of the localized feature of the surface $4f$ electron ($n_f \sim 1.0$), as shown in Table I, the $4f^0$ configuration weight in the initial state of the surface is very small. Accordingly, the probability of the $\underline{4d}4f^2$ final state is strongly suppressed in the surface $P(E_{ex})$ as compared with the bulk spectrum. As a result, the $[\underline{4d},4f^2(^3F)]^4G$ peak is weakened in the surface spectrum. On the other hand, there is large intensity of $\underline{4d}4f^3\underline{c}$ multiplets spread over the relatively higher energy region above 107 eV. Therefore, there is a strong admixture between the bulk and surface contribution to the RIPE spectra above $E_{ex}=107$ eV. This resonance feature is characteristic of the prethreshold region. In the giant resonance, the $\underline{4d}4f^2$ and $\underline{4d}4f^3\underline{c}$ multiplet structures in the intermediate state strongly mix with each other due to their very short lifetime. Therefore, if the excitation energy E_{ex} is tuned to the sharp ^4G peak, we can obtain the spectrum that includes a relatively larger bulk contribution. When ^4G is resonantly excited the large resonance enhancement of the f^1 peak with a dominant bulk contribution occurs. Simultaneously, the resonance enhancement of the bulk f^2 peak also occurs through the hybridization effect in the intermediate and final states.

Figure 3(d) shows the calculated bulk sensitivity in the lower side of the prethreshold region. The bulk sensitivity was obtained from the calculated RIPE spectra in Fig. 1(b) (see the caption). We can find, in fact, a sharp peak around 104.75 eV (A) and, unexpectedly, a dip around 108.5 eV (B). The former realizes the high bulk sensitivity around $E_{ex}=105$ eV as discussed above. Moreover, the latter indicates the existence of a ''surface-sensitive'' excitation energy range as in the case of the bulk. We can effectively probe the unoccupied bulk or surface $4f$ electronic states by the measurements at $E_{ex}\sim 104.75$ and 108.5 eV, respectively.

In Fig. 4, the RIPE spectra are measured at $E_{ex}\sim 104.7$, 108.5, and 121.5 eV. $E_{ex}=121.5$ eV causes the largest enhancement of the f^1 peak in the giant resonance as shown in Fig. 2. As mentioned above, the spectrum at 121.5 eV also contains considerable surface contribution. The f^2 peaks in the spectra at 108.5 and 121.5 eV are situated at lower energy side as compared with the one at 104.7 eV. The f^2 peak position in the spectrum at 104.7 eV is rather similar to that of the bremsstraulang isochromat spectrum (BIS) which is measured at 1486.6 eV.[10] BIS is a relatively bulk-sensitive technique due to a somewhat longer probing depth. This is an evidence of the higher bulk sensitivity of the spectrum measured around 105 eV. On the other hand, the surface-sensitive spectrum measured at 108.5 eV has a very small f^1 peak and the f^2 peak is shifted to the lower energy side by 0.8 eV as compared to the spectra at 104.7 eV. This ''surface-shift'' in f^2 peak is mainly caused by the difference in ϵ_f as shown in Table I. This result shows the localized character of the surface $4f$ electron and is consistent with the fact that many mixed-valent systems have a γ-like electronic structure in the surface region whereas they present a strongly α-like behavior in the bulk.[11,12]

In this short paper, we discussed the resonance effect on RIPE spectra at the $N_{4,5}$ prethreshold by comparison between experiment and calculation. The calculation well reproduced the observed features of RIPE spectra. The excitation energy dependence of the RIPE spectra can be clearly understood from the calculated $P(E_{ex})$ structures. We found that RIPE spectra measured at $E_{ex}\sim 105$ or 108.5 eV give the relatively bulk- or surface-sensitive spectrum, which gives direct and clear information about the unoccupied bulk- or surface-electronic states. This unique bulk- (or surface-) sensitivity is based on the following properties of the prethreshold resonance; (1) The observable difference in the intermediate-state energy of the bulk- and surface-resonance processes. This is caused by the difference in the parameters and $4f$ occupation of the intermediate states. (2) The narrower lifetime width of the multiplets that have exitonic feature at the prethreshold. As a result of the combination of (1) and (2), we can selectively excite the specific intermediate state (e.g., ^4G). Application of this method to other mixed-valent systems should be done systematically, then it will be a powerful tool for studying the nature of the surface $4f$ electronic states. Moreover, we can extract more reliable information about bulk $4f$ electronic states from RIPE spectra.

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