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Surface and bulk 4f-photoemission spectra of $CeIn_3$ and $CeSn_3$

H.-D. Kim
Department of Physics, Tohoku University, Sendai 980-77, Japan

O. Tjernberg
Material Physics, Royal Institute of Technology, S-10044, Stockholm, Sweden

G. Chiaia
INFM-Dip. Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133, Milano, Italy

H. Kumigashira and T. Takahashi
Department of Physics, Tohoku University, Sendai 980-77, Japan

L. Duò
INFM-Dip. Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133, Milano, Italy

O. Sakai and M. Kasaya
Department of Physics, Tohoku University, Sendai 980-77, Japan

I. Lindau
Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Sölvegatan 14 S-223 62 Lund, Sweden

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Resonant photoemission spectroscopy was performed on $CeIn_3$ and $CeSn_3$ at the $4d$-$4f$ and $3d$-$4f$ core thresholds. Using the different surface sensitivity between the two photon energies, surface and bulk $4f$-photoemission spectra were derived for both compounds. With the noncrossing approximation of the Anderson impurity model, the $4d$-$4f$ resonant spectra together with the surface and bulk spectra were self-consistently analyzed to obtain the microscopic parameters such as the $4f$-electron energy and the hybridization strength with conduction electrons. The result shows a substantial difference in these parameters between the surface and the bulk, indicating that it is important to take into account the surface effect in analyzing photoemission spectra of Ce compounds. It is also found that the $4f$ surface core-level shift is different between $CeIn_3$ and $CeSn_3$. [S0163-1829(97)05327-7]

I. INTRODUCTION

The valence-band photoemission spectroscopy (PES) of Ce metal and its compounds has played an important role in understanding their electronic structures.[1,2] Using the Gunnarsson-Schönhammer (GS) method[3] or the noncrossing approximation[4] (NCA) of the Anderson impurity model,[5] the low-energy thermodynamic properties are well explained with the same parameters used in the analysis of the high-energy valence-band PES spectra. In comparing the valence-band PES spectra with the GS or NCA calculations, it is necessary to extract only the $4f$-electron contribution to the valence band. For this purpose, $4d$-$4f$ resonant PES has been widely used.[1] Recently, it has been reported that in homogeneously mixed-valent (α-like) Ce compounds, the $3d$-$4f$ resonant PES spectrum is different from the $4d$-$4f$ resonant PES spectrum and there is an angular and kinetic-energy dependence of the Ce $3d$ core-level PES spectrum.[6] These facts were explained by the difference between the surface and bulk electronic structure of these compounds, and the analysis of the Ce $3d$ spectrum shows that the $4f$ occupancy at the surface is close to unity (γ-like).[6] The direct comparison of the bulk-sensitive $3d$-$4f$ spectrum with the surface-sensitive $4d$-$4f$ spectrum of α- and γ-Ce metal also led to the same conclusion.[7] Furthermore, the detailed analysis of the Ce $3d$ spectrum, the valence-band spectrum, and the bremsstrahlung isochromat spectrum of α- and γ-Ce metal, using the GS scheme with the same parameters except for the surface-to-bulk emission ratio, shows that it is necessary to consider the surface contribution, in particular for the valence-band PES where the surface component is comparable to the bulk one.[8]

In this paper, we present the $4d$-$4f$ and $3d$-$4f$ resonant PES spectra of $CeIn_3$ and $CeSn_3$. $CeIn_3$ is a γ-like compound that shows the normal Curie-Weiss susceptibility well above the Néel temperature T_N ($=10.2$ K),[9] while $CeSn_3$ is an α-like valence fluctuating system.[10,11] These compounds are isostructural (cubic $AuCu_3$ structure) and completely miscible, hence their alloy system has been widely investigated in order to study the valence instability, the magnetic behavior, and the electronic properties.[12–17] Thus, the resonant PES study of these compounds may be useful to understand their electronic structures and provide another opportunity to study how large the surface effect is on the f-electron spectrum of Ce compounds. The obtained $4d$-$4f$ and $3d$-$4f$ resonant spectra are quite different from each other even for

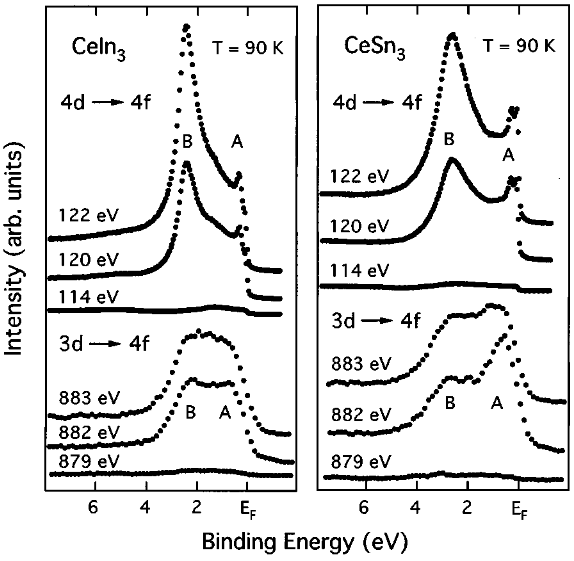

FIG. 1. The $4d$-$4f$ and $3d$-$4f$ resonant PES spectra of $CeIn_3$ (left panel) and $CeSn_3$ (right panel) at several photon energies at $T=90$ K. Peaks A and B correspond to the f^1 and f^0 final states, respectively.

γ-like $CeIn_3$. Assuming that this difference is mainly due to the difference between the surface and bulk electronic structures, we derived the surface and bulk $4f$-electron removal spectra from these two resonant spectra, and performed the analysis within the NCA method.

II. EXPERIMENT

Polycrystalline $CeIn_3$ and $CeSn_3$ were prepared by tri-arc melting under argon atmosphere. High-purity Ce (99.9% pure), In, and Sn (99.999%) in the respective composition ratio were used as starting materials. The obtained samples were characterized by x-ray diffraction and found to be of single phase.

PES measurements were performed at the soft-x-ray beam line 22 at the MAX Synchrotron Radiation Laboratory in Lund in normal emission geometry. The beamline is equipped with a modified SX-700 plane grating monochromator and a 200-mm mean radius hemispherical electron energy analyzer with a multichannel plate detector.[18] An overall energy resolution in the full width at half maximum (FWHM) of about 0.1 and 0.7 eV was achieved at the Ce $4d$-$4f$ ($\sim$120 eV) and Ce $3d$-$4f$ ($\sim$880 eV) thresholds, respectively. The samples were cleaned by scraping with a diamond file under vacuum (base pressure 7×10^{-11} mbar) immediately before the measurements. The samples were continuously kept at $\sim$90 K during the scraping and measurements in order to prevent the segregation of impurities from the bulk. Sample cleanliness has been checked by the O $1s$, C $1s$, and O $2p$ photoelectron spectra.

III. RESULTS AND DISCUSSION

Figure 1 shows the $4d$-$4f$ and $3d$-$4f$ resonant spectra of $CeIn_3$ and $CeSn_3$ at several photon energies. All spectra are normalized to the photon flux. The $4d(3d)$-$4f$ spectrum with $h\nu=114(879)$ eV shows the off-resonance spectrum and its intensity is very weak in comparison with the corresponding on-resonance spectra at $h\nu=120(882)$ and 122(883) eV, indicating that the non-$4f$ contribution is almost negligible in the on-resonance spectra. All on-resonance spectra consist of two main peaks; one (A) is near the Fermi energy (E_F) and the other (B) is at about 2.5 eV from E_F. Peaks A and B are assigned to the f^1 and f^0 final states, respectively.[1] The intensity ratio of A to B is related to the hybridization strength between the $4f$ electron and the conduction electron.[3,4] Both the $4d$-$4f$ and $3d$-$4f$ resonant spectra show that this intensity ratio is much larger in $CeSn_3$ than in $CeIn_3$, suggesting that the hybridization strength in $CeSn_3$ is stronger than that in $CeIn_3$. In the $4d$-$4f$ resonant spectra, peak A consists of two subpeaks, which are more clearly seen in $CeSn_3$. These two subpeaks are assigned to the tail of the Kondo resonance peak and its spin-orbit replica.[2,4] The intensity ratio between these two peaks is also related to the hybridization strength between the $4f$ electron and the conduction electron as illustrated by Patthey *et al.*[2] We find that the intensity of the tail of the Kondo resonance of $CeSn_3$ is stronger than that of $CeIn_3$.

Comparing the two on-resonance spectra at slightly different photon energies, we observe the change of the intensity ratio of A to B in both $4d$-$4f$ and $3d$-$4f$ resonant spectra. The intensity of peak A is more enhanced at lower photon energy than that of peak B and vice versa at higher photon energy. This photon-energy dependence of resonant spectra was also observed in other Ce compounds[1,19] and has been ascribed to the different intermediate states of the f^0 and f^1 final states.[20] Besides this photon-energy dependence, there is also a striking difference between the $4d$-$4f$ and $3d$-$4f$ resonant spectra. The intensity of peak A of the $3d$-$4f$ spectra is larger than that of the $4d$-$4f$ spectra in both compounds. In the $3d$-$4f$ spectrum, the photoelectron kinetic energy ($\sim$880 eV) is much higher than that of the $4d$-$4f$ spectrum ($\sim$120 eV), thus the surface contribution to the spectra is expected to be relatively small. When we assume that this difference is due to the difference of the surface-to-bulk ratio, we may extract surface and bulk components from the two resonant spectra.[7,21]

Providing that the surface contribution comes from the topmost Ce layer and the photoelectrons are emitted in the normal direction to the surface as expected from the present experimental setup, the surface-to-bulk emission ratio is given by $\exp(d/\lambda)-1$, where d is the thickness of the surface layer and λ is the electron escape depth at a given kinetic energy. Using the formula for the electron escape depth by Tanuma, Powell, and Penn,[22] we obtain the values of λ for the $4d(3d)$-$4f$ resonant spectra. The values of d are assumed to be equal to the lattice parameters (4.69 Å for $CeIn_3$, 4.72 Å for $CeSn_3$),[13] since $CeIn_3$ and $CeSn_3$ crystallize in a cubic $AuCu_3$ structure. From these values for $CeIn_3$ and $CeSn_3$, the surface-to-bulk emission ratio for the $4d(3d)$-$4f$ resonant spectra is calculated to be 1.20(0.24) and 1.33(0.26), respectively. Since there is a photon-energy dependence in the resonant spectra, we must choose the photon energies in such a way that the intensity ratio of A to B shows the same behavior.[23] Thus, we selected the photon

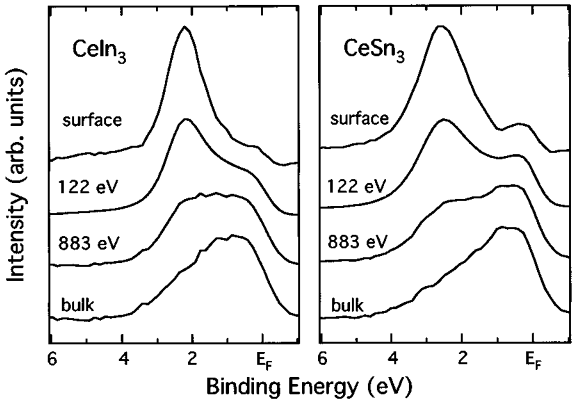

FIG. 2. The surface and bulk $4f$-electron spectra derived from the two resonant spectra, compared with the resonant PES spectra at the photon energies $h\nu = 122$ and 883 eV, for CeIn$_3$ (left panel) and CeSn$_3$ (right panel). The inelastic electron background and the off-resonance spectra are subtracted. The $4d$-$4f$ spectra are broadened by a Gaussian to enable the comparison with the $3d$-$4f$ spectra at equal instrumental resolution.

energies $h\nu = 122$ and 883 eV, where the intensity ratios of A to B are small but the $4f$ signal is strong. In addition, the $4d$-$4f$ spectra were broadened by a Gaussian in order to take into account the poorer experimental resolution in the $3d$-$4f$ spectra.

Figure 2 shows the derived surface and bulk spectra together with the measured resonant spectra at $h\nu = 122$ and 883 eV after the subtraction of the inelastic electron backgrounds and the off-resonance spectra by the usual method.[1] The derived surface and bulk spectra are very different from each other as expected from the resonant spectra. Comparing the surface and bulk spectra, we find that the effective hybridization is smaller and the position of the $4f$ electron is farther from E_F at the surface than in the bulk.

After extracting the surface and bulk $4f$-electron spectra, we tried to analyze the spectra using the NCA calculations with the same parameter set for each compound. According to the previous study,[1] we first tried to fit the $4d$-$4f$ resonant spectra without considering the surface effect. For γ-like CeIn$_3$, it was possible to fit the spectrum with reasonable parameters. However, for α-like CeSn$_3$, it was rather difficult to reproduce the experimental spectrum. As a matter of fact, there are two independent methods to estimate the hybridization strength between the $4f$ electron and the conduction electron from a $4f$-electron removal spectrum. The first one takes into account the intensity ratio between the f^1 and f^0 peaks. The larger this intensity ratio is, the stronger the hybridization.[1,3] The second method is the investigation of the $4f$ signal near E_F, which consists of the tail of the Kondo resonance peak and its spin-orbit replica. As the hybridization strength increases, the intensity of the tail of the Kondo resonance is enhanced drastically while there is little change in its spin-orbit replica.[2] For CeSn$_3$, it was impossible to meet these two constraints. When we reproduce the shape of the $4f$ signal near E_F, the intensity of the f^1 peak becomes much larger than that of the experiment. This fact suggests that the incorporation of the surface contribution is inevitable, because the surface contribution would reduce the intensity of the f^1 peak.

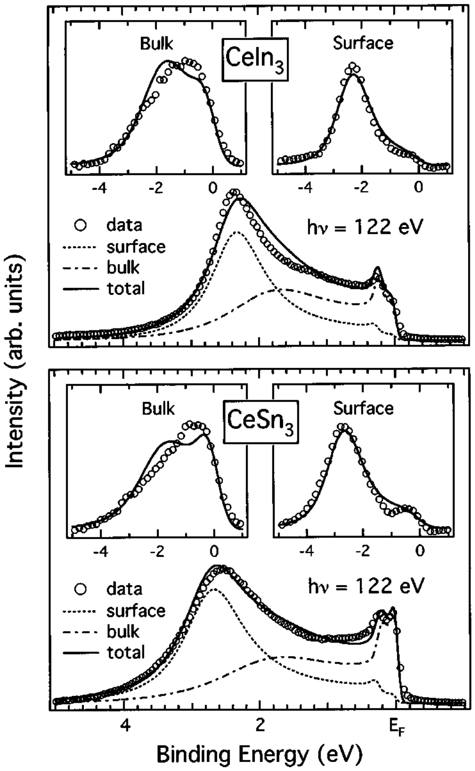

FIG. 3. Comparison of the $4d$-$4f$ resonant PES spectra with the NCA calculation for CeIn$_3$ (upper panel) and CeSn$_3$ (lower panel). Insets are for the surface and bulk $4f$-electron spectra. For the values of the relevant parameters, see Table I.

Figure 3 shows the comparison of the experimental $4f$ spectra and the calculated $4f$ spectra by the NCA method. The parameters in the calculation such as the f-electron energy ε_f, the effective hybridization $\Delta(0)$, the spin-orbit splitting $\Delta_{\rm SO}$, and the crystal-field splitting $\Delta_{\rm CF}$ are summarized in Table I. In calculating the spectrum, a Lorentzian with a width of 6 eV in FWHM was used to represent the conduction band. A previous inelastic neutron scattering study reported that the value of $\Delta_{\rm SO}$ of CeSn$_3$ is much larger than that of CeIn$_3$.[16] However, since it is quite peculiar that the value of $\Delta_{\rm SO}$ would deviate much from its free ion value and since there was no clear physical explanation for this behavior,[16] the value was fixed at $\Delta_{\rm SO} = 280$ meV in the

TABLE I. The parameters of the Anderson impurity model ($U \rightarrow \infty$) obtained from the spectral fit using the NCA calculation. Superscripts s and b represent surface and bulk, respectively. The errors of the parameters ε_f and $\Delta(0)$ are within 5%, not leading to any significant deviations of the spectra, and the values of $\Delta_{\rm SO}$ and $\Delta_{\rm CF}$ are fixed.

	ε_f^s (eV)	$\Delta(0)^s$ (meV)	ε_f^b (eV)	$\Delta(0)^b$ (meV)	$\Delta_{\rm SO}$ (meV)	$\Delta_{\rm CF}$ (meV)
CeIn$_3$	-2.15	47	-1.50	69	280	11.6[a]
CeSn$_3$	-2.40	63	-1.40	83	280	

[a] Reference 16.

calculation.[2] In the crystal field of a cubic crystal, the sixfold degenerate $4f^1$ ($^2F_{5/2}$) state should split into a Γ_7 doublet and a Γ_8 quartet state. According to the inelastic neutron scattering measurement,[16] $\mathrm{CeIn_3}$ shows an inelastic peak corresponding to the $\Gamma_7 \rightarrow \Gamma_8$ excitation. For $\mathrm{CeSn_3}$, however, the $4f^1$ state seems to recover its full degeneracy, $N=6$.[16,17] Thus, we included the crystal-field effect in the NCA calculation for $\mathrm{CeIn_3}$, but not for $\mathrm{CeSn_3}$.

As shown in Fig. 3, the surface 4f-electron spectra are well fitted in both compounds, but the fitting quality of the bulk spectra appears relatively poor. This is partially due to the fact that in the fitting procedure, relative importance was given to the reproduction of the 4f-electron spectrum at $h\nu=122$ eV. When we reduce the value of $|\varepsilon_f|$, a better quality fit of the bulk spectra may be obtained. In that case, however, the 4f signal near E_F at $h\nu=122$ eV is not well reproduced. One possible reason for this discrepancy may lie in the simple assumption that we made in the derivation of the bulk and surface spectra. Another possible reason is that the 3d-4f spectrum may be intrinsically different from the 4d-4f spectrum even when we consider the surface effect, because the atomic orbital involving the resonant process is different between the two cases.

The most notable result of the spectral fits is that the difference between the surface and bulk 4f-electron energies is large. As a result we find that the peak at about 2.5 eV from E_F, which has been used to estimate the bulk 4f-electron energy,[1] comes mostly from the surface and not the bulk. We also find in Table I that the 4f-electron energy difference in $\mathrm{CeSn_3}$ is larger than that in $\mathrm{CeIn_3}$. We may question that this is an artifact of the scraping procedure, which may create the different surface conditions between these compounds, for the surface core-level shift depends on the surface orientation. However, these compounds are isostructural and completely miscible,[12,13] so that we could expect that these compounds show similar mechanical properties. Thus, we neglect this effect for the present. According to the Johansson and Mårtensson model,[24] which explains the binding energy of a core level using the cohesive energies of Z and $(Z+1)$ elements and assuming the fully-relaxed core-hole state, the chemical shift of the surface core level is about 80% of that of the bulk one. Thus, the deviation from the prediction by their model seems to be unexpectedly large (-250%). However, the f-electron energy in the Anderson impurity model does not represent the energy of the fully relaxed final state in PES, but it is rather related with the initial state. Hence, we may ascribe the large difference in surface core-level shifts to the difference in the number of valence electrons between these two compounds, which may affect the Madelung potential and the density of the valence electrons, the values of which are crucial in determining the chemical shift but are difficult to estimate accurately.[25] In order to clarify this issue, a systematic PES investigation of various Ce compounds is necessary.

IV. CONCLUSION

We have performed 4d-4f and 3d-4f resonant PES on isostructural $\mathrm{CeIn_3}$ and $\mathrm{CeSn_3}$. The on-resonant PES spectra that represent mainly the 4f component in the valence band show a reasonable difference in the spectral shape between the two compounds, reflecting the physical properties of each compound. On the other hand, it was found that the 4d-4f and 3d-4f resonant PES spectra are significantly different from each other for both compounds. We analyzed the resonant PES spectra on the assumption that the photonenergy dependence is due to the surface effect since the electron escape depth of 4f photoelectrons would be substantially different at the two core thresholds (~120 and ~880 eV). We extracted the surface and bulk 4f-electron spectra from the two resonant PES spectra and compared them to the NCA calculation to obtain the microscopic physical parameters, such as the f-electron energy and the hybridization strength, for both the surface and the bulk separately. We found that the surface component shows a 4f level with higher binding energy and a reduced hybridization strength probably due to a smaller atomic coordination number at the surface. It is also noted that the surface core-level shift of these compounds is considerably different from each other. The present result shows that there is a substantial difference in the microscopic physical parameters between bulk and surface and also that it is essential to take into account the surface effect in analyzing the photoemission spectra, in particular, at the 4d-4f resonance.

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