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High-resolution Ce 3*d*-edge resonant photoemission study of $CeNi_2$

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Resonant photoemission (RPES) at the Ce $3d \rightarrow 4f$ threshold has been performed for α-like compound $CeNi_2$ with extremely high energy resolution (full width at half maximum <0.2 eV) to obtain bulk-sensitive $4f$ spectral weight. The on-resonance spectrum shows a sharp resolution-limited peak near the Fermi energy which can be assigned to the tail of the Kondo resonance. However, the spin-orbit side band around 0.3 eV binding energy corresponding to the $f_{7/2}$ peak is washed out, in constrast to the RPES spectrum at the Ce $4d \rightarrow 4f$ threshold. This is interpreted as due to the different surface sensitivity, and the bulk-sensitive Ce $3d \rightarrow 4f$ RPES spectra are found to be consistent with other electron spectroscopy and low energy properties for α-like Ce-transition metal compounds, thus resolving controversy on the interpretation of Ce compound photoemission. The $4f$ spectral weight over the whole valence band can also be fitted fairly well with the Gunnarsson-Schönhammer calculation of the single impurity Anderson model, but the detailed features show some dependence on the hybridization band shape and the Ce $5d$ resonant emission.

For several decades Ce metal and its compounds have attracted much attention because of their interesting physical properties, such as Kondo behavior, mixed valency, heavy fermion property, various magnetic states, and superconductivity, etc. Such properties are believed to originate from the interplay of a strong correlation between Ce $4f$ electrons and hybridization between $4f$ and conduction electrons, which is usually described by the periodic Anderson model.[1–4] Except for some materials with strong intersite interaction or at very low temperature where the coherence effect becomes important, the impurity version of the Anderson model (SIAM: single impurity Anderson model) is shown to be capable of describing many physical properties with a universal scale known as Kondo temperature.[4] It is now generally agreed that low-energy properties are well described by the Anderson model, but there is still controversy as to the interpretation of high-energy probes such as photoemission and inverse photoemission, which directly measure one-electron spectral weights.[1,2] Gunnarsson-Schönhammer calculation (GS: Ref. 3) and noncrossing approximation (NCA: Ref. 4) of the SIAM make it possible to compare directly a theoretical $4f$-electron spectrum with experimental photoemission data. Thus, in principle one can obtain model parameters of the SIAM for each compound from photoemission data, which can then be used to understand its low-energy properties. Resonant photoemission spectroscopy (RPES) at the Ce $4d \rightarrow 4f$ edge, x-ray photoelectron spectroscopy (XPS) for Ce $3d$ core-levels, and Bremsstrahlung isochromat spectroscopy (BIS), have been widely used for this purpose and shown to be quite successful for many Ce compounds.[1] On the other hand, Arko and co-workers[2] dispute this interpretation, claiming that the $4f$ weights of many Ce compounds measured by photoemission do not follow these schemes, in that $4d \rightarrow 4f$ RPES spectra of extremely α-like Ce compounds show some discrepancy with core-level XPS and BIS spectra, which has not been completely understood as yet.

One possible source of this discrepancy and controversy is the surface effect. From angle-dependent Ce $3d$ core-level XPS spectra and threshold-dependent RPES spectra of several α-like Ce compounds, Laubschat *et al.* proposed that surface electronic structures of those compounds are not α-like but γ-like,[5] which is now pretty well established.[6] Since the photon energy of the $4d\rightarrow4f$ threshold is so low that $4d\rightarrow4f$ RPES is quite surface sensitive, the discrepancy between an experimental $4d\rightarrow4f$ RPES spectrum and a theoretical one, which is obtained from parameters mainly determined by XPS and BIS, can be understood in terms of surface effects. In this context, $3d\rightarrow4f$ RPES is more desirable for examining bulk electronic structures of Ce compounds, because the escape depth of photoelectrons is longer. However, the resolution of a photon source around the $3d\rightarrow4f$ threshold has been much poorer than that at the $4d\rightarrow4f$ threshold, which rendered limited information.

In this work, we present $3d\rightarrow4f$ RPES spectra of very high Kondo temperature material CeNi$_2$ ($T_K>500$ K) with the extremely high experimental energy resolution [<0.2 eV full width at half maximum (FWHM)].[7] We found that the on-resonance spectrum shows a sharp resolution-limited peak near the Fermi energy (E_F) which can be assigned to the tail of the Kondo resonance. Comparison with a GS calculation of the SIAM shows good agreement between theory and experiment, thus high-resolution $3d\rightarrow4f$ RPES opens new opportunities to study *bulk* electronic structures of Ce compounds.

Polycrystalline CeNi$_2$ was prepared by arc melting of high-purity metals under an argon atmosphere. The structure and homogeneity were checked by x-ray diffraction. $3d\rightarrow4f$ RPES measurements of CeNi$_2$ were performed at the beamline BL25SU of the SPring-8. FWHM of the photon source around the $3d\rightarrow4f$ threshold is better than 200 meV and the temperature of the sample has been maintained at 30 K throughout the measurements. The SCIENTA SES200 electron analyzer was used to obtain an overall experimental resolution of ~0.2 eV FWHM. A clean sample surface was obtained by scraping *in situ* with a diamond file under the pressure of 4×10^{-10} Torr. Although scraping may induce disorder at the surface, accumulated experiences have shown that this effect is not so severe for metallic polycrystalline samples. E_F of the sample was referenced to that of a gold film deposited onto the sample substrate. $4d\rightarrow4f$ RPES measurements of CeNi$_2$ were also carried out at the beamline BL-3B of the Photon Factory, High Energy Accelerator Research Organization (KEK) in Tsukuba. FWHM of photon sources around the $4d\rightarrow4f$ threshold was about 30 meV and the overall experimental resolution of 40 meV was obtained with the SCIENTA SES200 electron analyzer. Scraping was incorporated for the sample cleaning under the base pressure better than 5×10^{-10} Torr, and all the measurements were done at 30 K. E_F of the sample was referenced to that of a gold film deposited onto the sample substrate and its position was accurate to better than 2 meV.

Figure 1 shows the valence-band RPES spectra of CeNi$_2$ around the Ce $4d\rightarrow4f$ threshold. All the spectra were normalized according to the photon flux. The spectra are overall consistent with previously published data.[1,8] As the photon energy changes, the spectrum does not show a remarkable resonant enhancement of the Ce $4f$ character in contrast to other Ce-non-transition-metal compounds. This fact was already noticed in the previous $4d\rightarrow4f$ RPES studies and was attributed to strong Ni $3d$ emission.[1,8] Furthermore, the photoionization cross section of Ni $3d$ electrons is strongly dependent on the photon energy around the $4d\rightarrow4f$ threshold,[9] thus it is hardly possible to extract a reliable Ce $4f$ removal spectrum using the conventional method.[10]

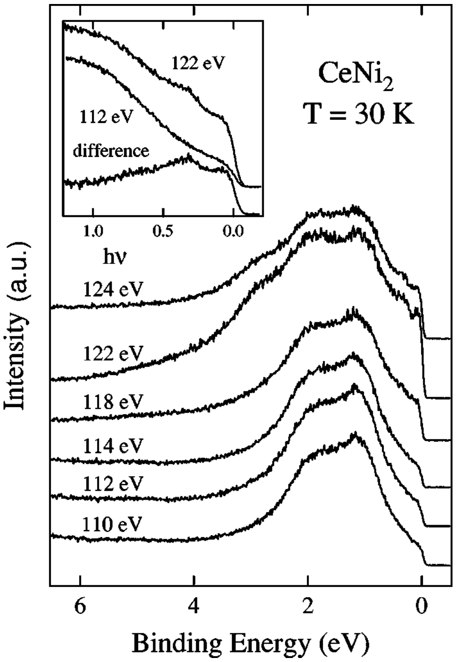

FIG. 1. Valence-band $4d\rightarrow4f$ RPES spectra of CeNi$_2$ at $T=30$ K. Inset shows detailed spectra near E_F.

In the on-resonance spectrum at $h\nu=122$ eV, we can see that two features grow up at about 3 eV and near E_F. The former could be assigned to an f^0 peak, and the latter to an f^1 one. In the inset of Fig. 1, the detailed spectra of the f^1 peak in the narrow region near E_F is shown. Similar to other Ce compounds, two features are enhanced at on resonance. As usual, we can assign the peak at the Fermi level to the tail of the Kondo resonance of the $f_{5/2}$ peak, while the one around 0.3 eV binding energy is its spin-orbit side band from the $f_{7/2}$ peak. The fact that that $f_{7/2}$ side band is clearly observed around 0.3 eV binding energy is somewhat inconsistent with the GS analysis (see below).

$3d\rightarrow4f$ RPES spectra of CeNi$_2$ are presented in Fig. 2. Contrary to the case of $4d\rightarrow4f$ RPES in Fig. 1, the Ce $4f$ character is dramatically enhanced in the on-resonance spectrum ($h\nu=881.4$ eV) in comparison with the off-resonance spectrum ($h\nu=868.1$ eV).[11] Especially, thanks to the extremely high resoultion, we can see a very sharp peak at E_F, whose position is limited by the experimental resolution. Thus, this peak is undoubtedly assigned to the tail of the Kondo resonance as was done for a lower-T_K CeSi$_2$ system with much better experimental resolution using the He I line.[12] We also observe a small hump around 1 eV binding energy and a broad feature around 3 eV binding energy. The broad feature around 3 eV binding energy probably originates from the f^0 character as generally accepted, but the origin of the 1 eV peak is a little controversial[13,14] and this will be discussed later.

Another interesting point is that we do not see any structure around 0.3 eV binding energy in the $3d\rightarrow4f$ on-resonance spectrum, which corresponds to the $f_{7/2}$ peak and is clearly noticeable in $4d\rightarrow4f$ RPES of Fig 1. This may be ascribed to the poorer energy resolution of $3d\rightarrow4f$ RPES

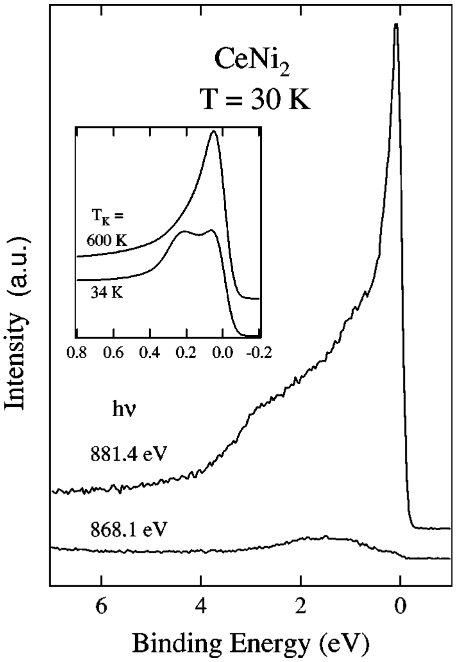

FIG. 2. Valence-band $3d \rightarrow 4f$ RPES spectra of CeNi$_2$ at $T = 30$ K. Inset shows the calculated near-E_F spectra depending on the Kondo temperature.

than that of $4d \rightarrow 4f$ RPES. However, we discard this possibility for the following reason. In order to see whether the line shape is due to the experimental resolution, we simulated a $4f$ spectrum of a low-T_K system, in which the $f_{7/2}$ peak is clearly resolved with 0.1 eV resolution (FWHM),[15] with our experimental resolution determined by fitting gold E_F spectrum. We then found that the highest peak position is around the center of the $f_{5/2}$ and $f_{7/2}$ peaks and the line shape is rather symmetric. These facts contradict the on-resonance spectrum in that the highest peak position is very close to E_F and the line shape is quite asymmetric as shown in Fig. 2, which implies that the intensity of the $f_{7/2}$ peak is smaller than in the $4d \rightarrow 4f$ RPES spectrum or the peak is indistinguishable from the tail of the Kondo resonance. In fact, according to the GS and NCA schemes of the SIAM, the line shape of the $f_{7/2}$ peak shows such a behavior as T_K increases.[16] The inset of Fig. 2 shows this change of near- E_F feature with T_K expected from the GS calculation. The upper (lower) curve simulates the experimental $3d \rightarrow 4f$ ($4d \rightarrow 4f$) RPES spectra, and these two curves are clearly incompatible. We conclude that the spin-orbit side band observed in previous high-resolution $4d \rightarrow 4f$ RPES and He II photoemission spectra of high-T_K Ce compounds, which was not well reproduced by GS and NCA calculations with parameters suitable for bulk physical properties, originates from the surface where the Ce $4f$ spectrum is more γ-like. This fact was also noticed by Kim *et al.* by analyzing $4d \rightarrow 4f$ and $3d \rightarrow 4f$ RPES spectra of CeIr$_2$.[14]

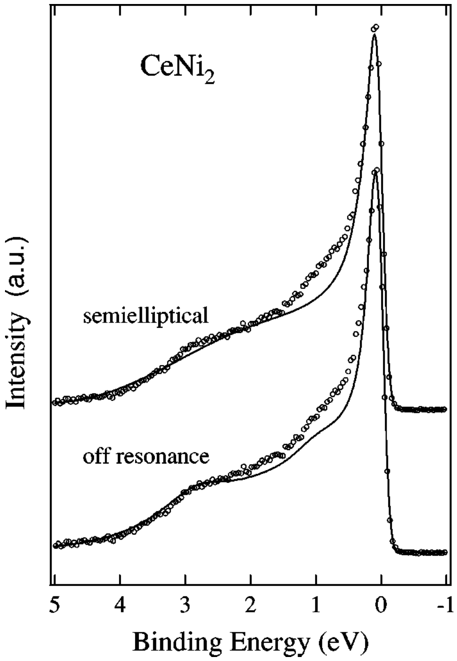

FIG. 3. Comparison of GS calculations (solid lines) of the SIAM with the Ce $4f$ spectrum (empty circles) of CeNi$_2$ derived from $3d \rightarrow 4f$ RPES spectra. The lower graph shows GS calculations using the off-resonance spectrum for $V(\varepsilon)^2$, the upper graph a semielliptical shape. For parameter values and detailed procedure, refer to text.

In order to see whether the bulk-sensitive $4f$ spectrum obtained from $3d \rightarrow 4f$ RPES of CeNi$_2$ is quantitatively explained by the SIAM, we have performed GS calculations which include spin-orbit splitting of the $4f$ level. Since it is not simple to separate surface and bulk contribution from the experimental data, for the moment we neglect the surface effect for the bulk-sensitive $3d \rightarrow 4f$ RPES spectra. Figure 3 shows the $4f$ spectrum derived from $3d \rightarrow 4f$ RPES spectra (empty circles) and the GS-calculation results (solid lines) employing the $4d \rightarrow 4f$ off-resonance spectrum (lower graph) and a semielliptical shape (upper graph) for the hybridization matrix elements $V(\varepsilon)^2$. For basis states we employed the lowest order f^0, f^1, and f^2, and the second-order f^0 states. The used parameter values are as follows: The $4f$-electron energy ε_f is -1.13, the spin-orbit splitting of the f level Δ_{so} is 0.28 eV, the hybridization strength averaged over the occupied valence band Δ_{av} is 89 meV, and the on-site Coulomb interaction between $4f$ electrons U is 6 eV, which give the $4f$-level occupancy $n_f = 0.78$. The static, $T = 0$ susceptibility $\chi(0)$ of CeNi$_2$ using the reference compound LuNi$_2$ and YNi$_2$, gives the estimates $n_f = 0.76$ and 0.83, respectively,[17] which is comparable to the present spectroscopic estimate. To compare the theoretical spectrum with experimental data, we first broadened the calculated spectrum with a Lorentzian of the width given by $0.01 + 0.20|E - E_F|$ eV, and then the spectral weight above E_F was removed using the method of Liu *et al.*,[18] and finally the resulting curve was convoluted by a Gaussian for experimental resolution.

The theoretical curves shown in Fig. 3 match the experimental data quite well, especially near the E_F region and the bottom of the valence band. This is taken as the evidence that the GS calculation with parameter values consistent with low-energy properties can reproduce the experimental photoemission spectra well even for high-T_K material CeNi$_2$. Although there might be concern that Ce $4f$ spectral weight extracted from $3d \rightarrow 4f$ resonant photoemission process may differ from the true $4f$ weight because of the decay Auger-matrix elements from the intermediate state, a recent theoretical calculation[19] shows that we can obtain quite faithful $4f$ weights, as long as we use photon energy in the lower multiplets of the Ce $3d_{5/2}$ edge, and this was the case in our experiments. The only region showing discrepancy between theory and experiment is around the binding energy of 1 eV. Similar 1 eV structure has been observed before in other Ce compounds, and its origin was a little controversial.[13,14] Lawrence *et al.*[13] claimed that the contribution of Ce $5d$ emission, whose position is around 1 eV, to the $4f$ spectrum is considerable (about 30%). Recent angle-resolved RPES studies of LaSb (Ref. 20) and La metal (Ref. 21) show that $4d\rightarrow 4f$ resonance also enhances valence bands due to La $5d$ emission, although its magnitude is much less than in Ref. 13. Such enhancement due to La $5d$ emission in La compounds was also observed in $3d\rightarrow 4f$ RPES.[22] However, the 1 eV structure could be reproduced by the GS calculations without considering $5d$ emission as demonstrated in the cases of α- and γ-Ce metal using realistic hybridization shape $V(\varepsilon)^2$ by Liu *et al.*,[18] and recently it was also proposed that a similar 1 eV structure for $\mathrm{CeIr_2}$ would be reproduced if realistic $V(\varepsilon)^2$ is used in the GS calculations.[14] Though the off-resonance spectrum may not be very realistic for $V(\varepsilon)^2$, our GS calculation presented in Fig. 3 using this off-resonance curve reveals a distinctive 1 eV structure, which is not observed in the calculation using a structureless semielliptical band, where all other paremeter values are kept the same (upper graph of Fig. 3). It strongly suggests that the hybridization between Ce $4f$ and Ni $3d$ electrons mainly contributes to the 1 eV structure, although the Ce $5d$ emission may also contribute. Thus it is quite essential to employ realistic $V(\varepsilon)^2$ in GS calculations in order to fully interpret experimental spectra.

In conclusion, we have performed high-resolution $4d\rightarrow 4f$ and $3d\rightarrow 4f$ RPES measurements of $\mathrm{CeNi_2}$. It was nearly impossible to extract a Ce $4f$ spectrum from the $4d\rightarrow 4f$ RPES spectra because of overlapping Ni $3d$ bands, but the $3d\rightarrow 4f$ RPES spectra with extremely high resolution provide a clear bulk-sensitive $4f$ spectrum. The experimental $4f$ spectrum thus obtained is well reproduced using a GS calculation of the SIAM. This is the first quantitative study on bulk-sensitive $4f$ weights of high T_K Ce materials, and it confirms the validity of a SIAM description for $\mathrm{CeNi_2}$. Similar studies on more α-like Ce compounds, such as $\mathrm{CeNi_5}$ and $\mathrm{CeRh_3}$, are clearly desirable to test the limit of the Anderson impurity model.

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[11] The off-resonance spectrum was taken at a somewhat lower photon energy, because around the usual value (875 eV: Ref. 6) there is strong enhancement of the Ni $3d$ character due to the Ni $2p_{1/2}\rightarrow 3d$ resonant process.

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