High-resolution Ce 3d-edge resonant photoemission study of CeNi$_2$

See-Hun Yang and S.-J. Oh
Department of Physics & Center for Strongly Correlated Materials Research, Seoul National University, Seoul 151-742, Korea

Hyeong-Do Kim
Department of Physics, University of Seoul, Seoul 130-743, Korea

Ran-Ju Jung
Japan Synchrotron Radiation Research Institute, Sayogun, Hyogo 6779-5198, Japan
and Department of Material Physics, Osaka University, Osaka 560-8531, Japan

A. Sekiyama, T. Iwasaki, and S. Suga
Department of Material Physics, Osaka University, Osaka 560-8531, Japan

Y. Saitoh
Japan Atomic Energy Research Institute, SPring-8, 1-1-1, Koto, Mikazuki, Sayo, Hyogo 079-5148, Japan

E.-J. Cho
Department of Physics, Chonnam National University, Kwangju 500-757, Korea

J.-G. Park
Department of Physics, Inha University, Inchon 402-751, Korea

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Resonant photoemission (RPES) at the Ce 3d $\rightarrow$ 4f threshold has been performed for $\alpha$-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 contrast 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 $\alpha$-like Ce-transition metal compounds, thus resolves 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, although the detailed features show some dependence on the hybridization band shape and (possibly) Ce 5d emissions.

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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 strong correlation between Ce 4f electrons and hybridization between 4f and conduction electrons, which is usually described by the periodic Anderson model. Although it is now generally agreed that low energy properties are well described by the Anderson model, 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. Gunnarsson-Schönhammer calculation (GS: Ref. 3) and noncrossing approximation (NCA: Ref. 4) of an impurity version of the model, i.e., the single impurity Anderson model (SIAM), make it possible to compare directly the 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 used for this purpose and shown to be quite successful for many Ce compounds. On the other hand, Arko and co-workers 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 $\alpha$-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 these 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, which is now pretty well established. Since the photon energy of the $4d \rightarrow 4f$ threshold is so low that $4d \rightarrow 4f$ RPES is quite surface sensitive, the discrepancy between experimental $4d \rightarrow 4f$ RPES spectrum and theoretical one, which is obtained from parameters mainly determined by XPS and BIS, can be understood in terms of surface effects. In this context, $3d \rightarrow 4f$ RPES is more desirable to examine bulk electronic structures of Ce compounds because the escape depth of photoelectrons is longer. However, the resolution of photon source around the $3d \rightarrow 4f$ threshold has been much poorer than that at the $4d \rightarrow 4f$ threshold, which rendered limited information.

In this work, we present $3d \rightarrow 4f$ RPES spectra of very high Kondo temperature material CeNi$_2$ ($T_K \sim 1000$ K) with the extremely high experimental energy resolution ($0.2$ eV full width at half maximum (FWHM)). We found that 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 $3d \rightarrow 4f$ 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 argon atmosphere. The structure and homogeneity were checked by x-ray diffraction. $3d \rightarrow 4f$ RPES measurements of CeNi$_2$ were performed at the beamline BL25SU of the SPring-8. FWHM of photon source around the $3d \rightarrow 4f$ threshold was better than 200 meV and the temperature of the sample was maintained at 30 K throughout the measurements. The SCIENTA SES200 electron analyzer was used to obtain an overall experimental resolution of $\sim 0.2$ eV. Clean sample surface was obtained by scraping in situ with a diamond file under the pressure of $4\times 10^{-10}$ Torr. $E_F$ of the sample was referenced to that of a gold film deposited onto the sample substrate. $4d \rightarrow 4f$ 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 $4d \rightarrow 4f$ 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 $5 \times 10^{-10}$ 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 $4d \rightarrow 4f$ threshold. All the spectra are normalized according to the photon flux. The spectra are overall consistent with early data, except for the difference of energy resolution. 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 poorer-resolution $4d \rightarrow 4f$ RPES study and was attributed to strong Ni $3d$ emission. Photoemission cross section of Ni $3d$ electrons is strongly dependent on the photon energy around the $4d \rightarrow 4f$ threshold, thus it is hardly possible to extract reliable Ce $4f$ removal spectrum using the conventional method.

In the on-resonance spectrum at $\hbar \nu = 122$ 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 on resonance. As usual, we can assign the peak at the Fermi level to the tail of 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 $f_{7/2}$ side band is clearly observed around 0.3 eV binding energy is somewhat inconsistent with the GS analysis (see below).

$3d \rightarrow 4f$ RPES spectra of CeNi$_2$ are presented in Fig. 2. Contrary to the case of $4d \rightarrow 4f$ RPES in Fig. 1, the Ce $4f$ character is dramatically enhanced in the on-resonance spectrum ($\hbar \nu = 881.4$ eV) in comparison with the off-resonance spectrum ($\hbar \nu = 868.1$ eV). Especially, thanks to the extremely high resolution, 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. 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 and this will be discussed later. We then found that the highest peak position is around $f/2$ and is clearly noticeable in $4d \rightarrow 4f$ RPES of Fig. 1. We first suspected this may be due to the poorer energy resolution of $3d \rightarrow 4f$ RPES than that of $4d \rightarrow 4f$ RPES, but we discarded this possibility for the following reason. In order to see whether the lineshape is due to the experimental resolution, we simulated a 4 $f$ spectrum of a low-$T_K$ system, in which the $f/2$ peak is clearly resolved with 0.1 eV resolution (FWHM) 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 $f/2$ and $f/2$ peaks and the lineshape is rather symmetrical. These facts contradict the on-resonance spectrum in that the highest peak position is very close to $E_F$ and the lineshape is quite asymmetric as shown in Fig. 2, which implies that the intensity of the $f/2$ 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 lineshape of the $f/2$ peak shows such a behavior as $T_K$ increases. 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 4$f$ spectrum is more $\gamma$-like. This fact was also noticed by Kim et al. by analyzing $4d \rightarrow 4f$ and $3d \rightarrow 4f$ RPES spectra of CeIr$_2$.

![Diagram](image)

FIG. 2. Valence-band $3d \rightarrow 4f$ RPES spectra of CeNi$_2$ at $T = 30$ K.

Another interesting point is that we do not see any structure around 0.3 eV binding energy in the $3d \rightarrow 4f$ on-resonance spectrum, which corresponds to the $f/2$ peak and is clearly noticeable in $4d \rightarrow 4f$ RPES of Fig. 1. We first suspected this may be due to the poorer energy resolution of $3d \rightarrow 4f$ RPES than that of $4d \rightarrow 4f$ RPES, but we discarded this possibility for the following reason. In order to see whether the lineshape is due to the experimental resolution, we simulated a 4$f$ spectrum of a low-$T_K$ system, in which the $f/2$ peak is clearly resolved with 0.1 eV resolution (FWHM) 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 $f/2$ and $f/2$ peaks and the lineshape is rather symmetrical. These facts contradict the on-resonance spectrum in that the highest peak position is very close to $E_F$ and the lineshape is quite asymmetric as shown in Fig. 2, which implies that the intensity of the $f/2$ 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 lineshape of the $f/2$ peak shows such a behavior as $T_K$ increases. 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 4$f$ spectrum is more $\gamma$-like. This fact was also noticed by Kim et al. by analyzing $4d \rightarrow 4f$ and $3d \rightarrow 4f$ RPES spectra of CeIr$_2$. In order to see whether the bulk-sensitive 4$f$ spectrum obtained from $3d \rightarrow 4f$ RPES of CeNi$_2$ is quantitatively explained by the SIAM, we have performed GS calculations which includes spin-orbit splitting of the 4$f$ level. Since it is not simple to separate surface and bulk contribution from the experimental data, we will neglect the surface effect for the bulk-sensitive $3d \rightarrow 4f$ RPES spectra here. Figure 3 shows the 4$f$ spectrum derived from $3d \rightarrow 4f$ RPES spectra (empty circles) and the GS-calulation 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 4$f$-electron energy $\varepsilon_f$ is -1.13, the spin-orbit splitting of the $f$ level $\Delta_{so}$ is 0.28 eV, the hybridization strength averaged over the occupied valence band $\Delta_{av}$ is 89 meV, and the on-site Coulomb interaction between 4$f$ electrons $U$ is 6 eV, which give the 4$f$-level occupancy $n_f = 0.78$. The static, $T = 0$ susceptibility $\chi(0)$ of CeNi$_2$ gives the estimates $n_f = 0.76$ and 0.83 depending on the reference estimate.
compound, 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 $0.01+0.20(E-E_F)\text{ eV}$, and then the spectral weight above $E_F$ was removed using the method of Liu et al., 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$_2$. 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. Lawrence et al. claimed that the contribution of Ce 5$d$ emission, whose position is around 1 eV, to the 4$f$ spectrum is considerable (about 30%).

Recent angle-resolved RPES studies of LaSb (Ref. 18) and La metal (Ref. 19) show enhancement of La 5$d$ emission at the $4d \rightarrow 4f$ resonance, although its magnitude is much less than claimed in Ref. 19. The enhancement of La 5$d$ emission in La compounds was also observed in 3$d \rightarrow 4f$ RPES. On the other hand, such 1 eV structure could be reproduced by the GS calculations without considering 5$d$ emission as demonstrated in the cases of $\alpha$- and $\gamma$-Ce metal using realistic hybridization shape $V(\varepsilon)^2$ by Liu et al. and recently it was also proposed that similar 1 eV structure for CeF$_3$ would be reproduced if realistic $V(\varepsilon)^2$ is used in the GS calculations. 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 distinctive 1 eV structure, which is not observed in the calculation using structureless semilatticidal band, where all other parameter values are kept the same (upper graph of Fig. 3). It strongly suggests that the hybridization between Ce 4$f$ and Ni 3$d$ electrons plays an important role for this 1 eV peak, although 5$d$ 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 4$d \rightarrow 4f$ and 3$d \rightarrow 4f$ RPES measurements of CeNi$_2$. It was nearly impossible to extract Ce 4$f$ spectrum from the 4$d \rightarrow 4f$ RPES spectra because of overlapping Ni 3$d$ bands, but the 3$d \rightarrow 4f$ RPES spectra with extremely high resolution provide a clear bulk-sensitive 4$f$ spectrum. The experimental 4$f$ spectrum thus obtained is well reproduced using a GS calculation of the SIAM.

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1. J. W. Allen et al., Adv. Phys. 35, 275 (1986).
2. J. J. Joyce et al., Phys. Rev. Lett. 68, 236 (1992); J. J. Joyce et al., Physica B 186-188, 31 (1993); also see Ref. 12 for brief review.
3. O. Gunnarsson and K. Schönhammer, Phys. Rev. B 28, 4315 (1983); 31, 4815 (1985).
4. N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B 36, 2036 (1987).
5. Laubschat et al., Phys. Rev. Lett. 43, 3137 (1990).
6. See, for review, L. Duò, Surf. Sci. Rep. 32, 233 (1998).
7. Y. Saitoh et al., J. Synchrotron Rad. 5, 542 (1998); A. Sekiyama et al., Solid State Commun. 111, 373 (1999).
8. J. J. Yeh and I. Lindau, Atomic Data and Nuclear Tables 32, 1 (1985).
9. We tried to extract surface and bulk Ce 4$f$ spectra from the 4$d \rightarrow 4f$ and 3$d \rightarrow 4f$ RPES spectra using the conventional method. The derived surface spectrum, however, shows strong negative intensity near $E_F$ probably due to the inappropriate extraction of Ce 4$f$ spectrum at the 4$d \rightarrow 4f$ threshold.
10. The off-resonance spectrum was taken at somewhat lower photon energy, because around the usual value (875 eV: Ref. 12) there is strong enhancement of the Ni 3$d$ character due to Ni 2$p_{1/2} \rightarrow 3d$ resonant process.
11. M. Garnier et al., Phys. Rev. Lett. 78, 4127 (1998).
12. J. M. Lawrence et al., Phys. Rev. B 47, 15 460 (1993).
13. H.-D. Kim et al., Phys. Rev. B 59, 12 294 (1999).
14. We could indeed observe the well-resolved $f_{7/2}$ peak in the 3$d \rightarrow 4f$ RPES of low-$T_K$ systems, when we improved the resolution to 0.1 eV.
15. D. Malterre, M. Grioni, and Y. Baer, Adv. Phys. 45, 299 (1996).
16. J. Sakurai, Y. Tagawa, and Y. Komura, J. Magn. Magn. Mater. 52, 205 (1985).
17. L. Z. Liu et al., Phys. Rev. B 45, 8934 (1992).
18. C. G. Olson et al., Phys. Rev. Lett. 76, 4265 (1996).
19. S. L. Molodtsov et al., Phys. Rev. Lett. 78, 142 (1997).
20. S. Suga et al., (unpublished).