Auger Effect in the High-Resolution Ce 3d-edge Resonant Photoemission

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Abstract

The bulk-sensitive Ce 4f spectral weights of various Ce compounds including CeFe2, CeNi2, and CeSi2 were obtained with the resonant photoemission technique at the Ce 3d-edge. We found the lineshapes change significantly with the small change of the incident photon energy. Detailed analysis showed that this phenomenon results primarily from the Auger transition between
different multiplet states of the Ce $3d_{5/2}4f^2$ (bar denotes a hole) electronic configuration in the intermediate state of the resonant process. This tells us that extra care should be taken for the choice of the resonant photon energy when extracting Ce $4f$ spectral weights from the Ce $3d$-edge resonant photoemission spectra. The absorption energy corresponding to the lowest multiplet structure of the Ce $3d_{5/2}4f^2$ configuration seems to be the logical choice.
I. INTRODUCTION

Investigations on the electronic structures of strongly correlated materials such as $d$ and $f$ electron systems have been very active lately.\textsuperscript{1,2} One of the perhaps oldest problems in this category is the origin of the $\alpha \leftrightarrow \gamma$ phase transition of Ce metal and its compounds, which has been studied for more than 50 years but still remains controversial.\textsuperscript{3–5} Photoemission spectroscopy, among various experimental techniques, is a very powerful tool that can directly probe the electronic structures of solids. Indeed in the case of Ce problem as well, the study of $4f$ spectral weights of various Ce compounds using resonant photoelectron spectroscopy (RPES) technique at the Ce 4$d$-edge contributed decisively to the understanding of this famous phase transition. This technique is necessary to enhance the $4f$ electron emissions and separate them from contributions of other conduction electrons,\textsuperscript{6} and utilizes the following process

$$4d^{10}4f^1 + \hbar \omega \rightarrow 4d^94f^2 \rightarrow 4d^{10}4f^0 + \text{photoelectron}.$$  

The conventional wisdom that came out of these studies, at least until early 1990’s, was as follows; The major factor distinguishing between $\alpha$ and $\gamma$ phases of Ce and its compounds is the strength of the hybridization between Ce $4f$ level and the conduction bands, and the disappearance of the local magnetic moment in the $\alpha$ phase results from the Kondo phenomenon of the singlet formation due to the hybridization of a localized $4f$ electron with conduction electrons, and not from the promotion of the $4f$ electron to the empty state above the Fermi level.\textsuperscript{3–5}

After the high resolution RPES was developed in the early 1990’s, however, some groups questioned this conventional wisdom and proposed a new interpretation of the $4f$ spectral weights of Ce compounds.\textsuperscript{7,8} The main point of those groups was that the temperature or the material dependence of the $4f$ spectral weights of Ce compounds near the Fermi level, which had been interpreted as the tail of the Kondo resonance,\textsuperscript{9} did not follow the Kondo scenario which stipulates that the Kondo temperature is the universal controlling parameter that
determines the strength of the Kondo resonance near the Fermi level in different materials or at different measuring temperatures. This controversy generated many more careful studies on the 4f spectral weights of various Ce compounds by several research groups, some utilizing RPES technique and others using ordinary ultraviolet photoemission (UPS) technique with He\textsubscript{I} (h\nu = 21.2 eV) and He\textsubscript{II} (h\nu = 40.8 eV) sources.

Most of these later studies also supported Kondo resonance scenario, but one important issue which has not been settled so far is the surface effect and how to separate the surface from the bulk contributions. Since the electron kinetic energy at the Ce 4d-edge RPES is about 120eV, and the electron mean free path at this kinetic energy is only about 5\AA, the surface contribution in the 4f spectral weights obtained with 4d-edge RPES technique is expected to be very much significant, even larger than the bulk in some cases. The situation with the ordinary UPS data with He\textsubscript{I} (h\nu = 21.2 eV) and He\textsubscript{II} (h\nu = 40.8 eV) sources is not much different. Hence to compare quantitatively the experimental photoemission spectra with those expected from the Kondo temperature of bulk materials, it is imperative to be able to extract the bulk contributions from the experimental data. Many approaches have been tried with the Ce 4d-edge RPES or ordinary UPS data, but the results were not conclusive enough since each method has its own drawbacks and uncertainties.

Recently a powerful new method to extract reliable bulk Ce 4f spectral weights has become possible thanks to the advent of the new beamline at SPring-8, Japan. It has been well-known that we can reduce the surface contribution in photoemission spectra by using high energy photon source. For example, if around 880eV photon source is used in RPES, the electron mean free path of the photoelectrons from Ce 4f levels will be about 20\AA. Since those 880eV photon energies can excite a Ce 3d core-electron to an empty 4f level (Ce 3d absorption edge), the 4f spectral weight is also enhanced due to the resonance phenomenon as in the case of Ce 4d-edge RPES. Hence we can obtain much more bulk-sensitive Ce 4f spectral weights by using those high photon energies in this so-called Ce 3d-edge RPES technique. In fact, this technique had been already tried more than 10 years ago, but the energy resolution in the Ce 3d-edge RPES at that time was not good enough
to give conclusive results. Recently, Sekiyama et al. succeeded to obtain the total energy resolution including energy analyser at the Ce 3d edge photon source less than 100meV with high photon flux in the undulator beamline of SPring-8 and study high-resolution bulk-sensitive Ce spectral weights in CeRu$_2$.\textsuperscript{20} This opened up a new possibility to extract reliable bulk-sensitive spectral weights in many interesting Ce compounds, and several papers have already appeared utilizing this Ce 3d-edge RPES technique.\textsuperscript{20–22}

However, in the course of this study, we realized that the experimental photoemission data depends sensitively on the exact incident photon energy near the Ce 3d-edge, and the difference of spectral lineshape is significant enough to affect data interpretation. Also the new Ce 3d-edge RPES data were found to be not completely consistent with the old data taken in early 1990’s, even after the difference of the energy resolutions is taken into account. To derive reliable conclusions from the Ce 3d-edge RPES data, therefore, it is necessary to understand the origin of these differences and changes. This paper is an attempt to understand the origin of these phenomena by systematically studying Ce 3d-edge RPES of several Ce compounds. We will show in this paper data on CeFe$_2$, CeNi$_2$, and CeSi$_2$ only, although we studied many more Ce compounds which gave fully consistent results with the conclusion of this paper. The three Ce compounds to be discussed here have various Kondo temperature, the universal parameter which controls many physical properties of Ce compounds in the Kondo resonance scenario. The Kondo temperatures of intermetallic compounds CeFe$_2$ and CeNi$_2$ are larger than about 500 K, and that of CeSi$_2$ compound is about 45 K.\textsuperscript{4,5} This paper will mainly focus on the general phenomena of the Ce 3d-edge RPES, and the electronic structures of individual compounds will be discussed in separate publications.\textsuperscript{23,24}

II. EXPERIMENTAL

Polycrystalline samples of CeFe$_2$, CeNi$_2$, and CeSi$_2$ were made by the arc melting method under Ar gas environment with constituent elements Ce, Fe, Ni, and Si whose purity was
better than 99.9%. The homogeneity of samples was checked after annealing with x-ray diffraction.

Resonant photoemission spectra of the valence bands at various photon energies near the Ce 3d-edge (hν ∼ 880 eV) along with the Ce 3d-edge x-ray absorption spectrum (XAS) were obtained at the beamline BL25SU in the SPring-8 of Japan. The base pressure of an analysis chamber was about 3 × 10⁻¹⁰ mbar or better. The samples were scraped with a diamond file to get clean surfaces, and every time the cleanness of sample surface was checked with the O 1s core-level spectrum. If the oxygen contamination peak was found noticeable in O 1s core-level spectrum, the samples were scraped again with the diamond file. All spectra were measured at the temperature of 20 K, and the scraping was also done at 20 K. The XAS measurements were done by the total electron yield mode, and the energy resolution was about 80 meV. Scienta 200 analyzer was used for the electron energy analysis for PES measurements, and the total resolution of the PES spectra was better than 100 meV.

**III. DATA AND DISCUSSIONS**

Fig. 1 shows the Ce M_V XAS data representing 3d⁵/₂ → 4f transition for CeFe₂, CeNi₂, and CeSi₂ compounds. The 3d⁵/₂ XAS of Fig. 1 consists of the main peak structure near hν = 882 eV, and the satellite peak near hν = 887 eV. The main peak structure comes from "3d⁵f⁰ → 3d⁴f²" transition, and the satellite peak "3d⁵f⁰ → 3d⁶f⁰" transition. The mark of " " means approximate interpretation, since the complete eigenstate of each peak is composed of many body configurations. The lineshape of the main peak near 882 eV is primarily determined by the multiplet structures of the 3d⁴f² electronic configuration, where the underline represents a hole. At the bottom of the figure is shown the theoretically expected XAS line spectrum, which is calculated by considering all the multiplets of the 3d⁵/₂4f² electronic configuration along with the appropriate transition probability from the ground state. We can see that the theoretical calculation compares favorably with the
experimental XAS data, especially for the case of CeSi$_2$, although we can also notice that the details of the main peak lineshape and the satellite peak intensity near 887eV change somewhat depending on the compounds. We will deal with this phenomenon and its implication on the electronic structures systematically in a separate publication. In this figure, the symbols A to G designate the incident photon energies used to obtain the 4f spectral weights with the Ce 3d-edge RPES to be shown in subsequent figures.

Fig. 2 represents RPES spectra near the Fermi level of CeFe$_2$ obtained with various incident photon energies corresponding to the symbols from A to G in Fig. 1. All through these photon energies the Ce 4f spectral weights are resonantly enhanced by the following process.

$$3d^{10}4f^1 + h\omega \rightarrow 3d^94f^2 \rightarrow 3d^{10}4f^0 + \text{photoelectron.}$$

Since the contribution from the Ce 4f emissions is at least ten times larger than those from other conduction electrons at these resonance energies, we can safely neglect the other conduction electron contributions and consider the spectra of fig. 2 as the Ce 4f spectral weights near the Fermi level, as in the case of Ce 4d-edge RPES. However, the bulk contribution of Ce 4f spectral weights of Fig. 2 is much larger than that of 4d edge RPES, since the electron mean free path at 3d → 4f transition energies is much longer.

The spectra in Fig. 2 consist of a peak near the Fermi level and a shoulder at about 2eV. The shoulder near 2eV comes from the $f^1 \rightarrow f^0$ transition, whereas the peak near the Fermi level comes from $f^1 \rightarrow f^0\overline{c}$ transition (c means the hole in the conduction band) which corresponds to the tail of the Kondo resonance peak. The detailed analysis on those peaks and their relation to the electronic structures of CeFe$_2$ have been dealt with in other papers. Here we focus on the change of the 4f spectral lineshapes depending on the incident photon energy. We clearly see that as the photon energy is increased from A (881.76eV) to F (882.48eV), which is only 0.72eV apart, the width of the peak near the Fermi level is significantly broadened. To see these changes of spectral weights more quantitatively, we subtracted the spectrum at A from data taken at higher photon energies.
after normalizing each spectrum at its maximum intensity. The resulting difference spectra at various photon energies are shown in Fig.3.

We find two noticeable features in every difference spectrum of Fig.3 — a broad peak below the Fermi level $E_F$ and a sharp dip at $E_F$. The maximum of the broad peak moves to the high binding energy side as the incident photon energy is increased. In fact, we note that the binding energy of the maximum position is exactly the same as the difference of two incident energies, which is indicated by the arrows. This tells us the kinetic energy of the broad peak remains the same regardless of the incident photon energy, a telltale signature of Auger emission. Hence, we can conclude that this broad peak results from the Auger transition, and that the apparent change of the spectral lineshapes depending on the incident photon energy is due to these Auger emissions overlapping the resonant $4f$ photoemissions. This Auger process must be the Coster-Kronig type between different multiplets of the $3d^94f^2$ configuration in the intermediate state of RPES.

To obtain genuine Ce $4f$ spectral weights from RPES data, therefore, it is necessary to avoid the contribution from these overlapping Auger emissions. The best way to achieve this is probably to take the spectrum at the incident photon energy corresponding to the lowest multiplet of the intermediate state. Indeed, we can see in the figure that the difference spectrum between B and A is nearly flat, implying that the spectral shape is nearly identical for data taken near the lowest multiplet. We have also confirmed that the spectra taken at incident photon energies slightly below A remain identical in lineshapes as that of A. This fact gives us an important lesson in extracting bulk-sensitive Ce $4f$ spectral weights using the $3d$-edge RPES technique — that is, it is dangerous to use the incident photon energy which simply gives maximum resonance effect (such as peak E in Fig.1), since at that energy the spectra might be contaminated with overlapping Auger emissions. It is instead best to choose the incident photon energy as low as possible which still gives appreciable resonance effect. Some of the previous Ce $3d$-edge RPES experiments may have been performed at the photon energy of maximum resonance, in which case the data have to be interpreted with caution. This interpretation on the origin of the lineshape change with the incident
photon energy can also explain the dip structure near $E_F$ shown in Fig.3. Because of the Auger transition between multiplets, the intensity of the Kondo resonance peak near $E_F$ will be reduced while some intensities move to higher binding energy side. Therefore if each spectrum is normalized to its maximum height before subtraction, as we did in our case, a dip will show up near the Fermi level with negative intensity in the difference spectra.

This phenomenon of overlapping Auger emissions in the Ce 3$d$-edge RPES spectra is not limited to the particular case of CeFe$_2$. In Fig. 4 and Fig. 5 are shown the Ce 3$d$-edge RPES data for CeNi$_2$ and CeSi$_2$, respectively, taken at various incident photon energies. Again, we see that they both show changes of spectral shapes depending on the photon energy, similar to the case of CeFe$_2$. The two spectra of CeNi$_2$ in Fig.4 are obtained with the incident photon energy of 882.34eV (E) and 881.54eV (A), which are very close to each other and roughly corresponds to two maximum points of 3$d_{5/2}$ XAS spectrum of CeNi$_2$ in Fig. 1. But these two 4$f$ spectral weights have appreciably different shapes in that the spectrum at photon energy E shows a fairly strong peak around 0.8eV binding energy, which becomes very weak or absent in the spectrum A. To understand the origin of this change of spectral shape, we again took the difference spectrum of the two and showed it at the bottom of Fig. 4. We can see in this difference spectrum a broad peak with its maximum around 0.8eV binding energy, which is exactly the difference of the photon energy and therefore corresponds to the constant kinetic energy feature. This tells us that in this case of CeNi$_2$ as well the origin of this phenomenon is the same as the case of CeFe$_2$ discussed earlier, and the overlapping Auger emissions between different multiplets of 3$d^94f^2$ intermediate state contribute to the lineshape change with the incident photon energy. The CeSi$_2$ spectra shown in Fig. 5 gives the same story, although the phenomenon does not look as pronounced as in the case of CeNi$_2$. 
IV. CONCLUSION

In the newly-developed Ce 3d-edge resonance photoemission technique for the study of bulk electronic structures of Ce compounds, the spectral shapes were found to depend sensitively on the incident photon energy. By analyzing Ce 3d-edge RPES valence band spectra of CeFe$_2$, CeNi$_2$, and CeSi$_2$ compounds systematically, we showed that this phenomenon originated from the Auger transition between different multiplet structures of 3d4f$^2$ electronic configuration in the intermediate state of the resonance process. Although we only showed the data on CeFe$_2$, CeNi$_2$, and CeSi$_2$ in this paper, we found similar results for other Ce compounds as well, and expect this phenomenon to be universal for any Ce compounds. Hence, when the Ce f spectral weights are obtained with the Ce 3d-edge RPES technique, it is very important to avoid these overlapping Auger emissions contributing to the spectra. The most logical choice of the incident photon energy must be that corresponding to the lowest multiplet of the 3d-edge x-ray absorption spectra.

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REFERENCES

1 J.M. Lawrence, P.S. Riseborough, and R.D. Parks, Rep. Prog. Phys. 44, 1 (1981).

2 G.R. Stewart, Rev. Mod. Phys. 56, 755 (1984).

3 W.H. Zachariasen, Phys. Rev. 76, 301 (1949); L. Pauling, J. Chem. Phys. 18, 145 (1950).

4 J.W. Allen, S.-J. Oh, O. Gunnarsson, K. Schonhammer, M.B. Maple, M.S. Torikachvili, and I. Lindau, Adv. Phys. 35, 275 (1986).

5 D. Malterre, M. Grioni, and Y. Baer, Adv. Phys. 45, 299 (1996).

6 J.W. Allen, S.-J. Oh, I. Lindau, J.M. Lawrence, L.I. Johansson, and S.B. Hagstrom, Phys. Rev. Lett. 46, 1100 (1981).

7 J.J. Joyce, A.J. Arko, J. Lawrence, P.C. Canfield, Z. Fisk, R.J. Bartlett, and J.D. Thompson, Phys. Rev. Lett. 68, 236 (1992).

8 R.I.R. Blyth, J.J. Joyce, A.J. Arko, P.C. Canfield, A. B. Andrews, Z. Fisk, J.D. Thompson, R.J. Bartlett, P. Riseborough, J. Tang, and J.M. Lawrence, Phys. Rev. B 48, 9497 (1993).

9 O. Gunnarsson and K. Schonhammer, Phys. Rev. Lett. 50, 604 (1983); Phys. Rev. B 28, 4315 (1983).

10 D. Malterre, M. Grioni, P. Weibel, B. Dardel, and Y. Baer, Phys. Rev. Lett. 68, 2656 (1992).

11 M. Grioni, P. Weibel, D. Malterre, Y. Baer, and L. Duo, Phys. Rev. B 55, 2056 (1997).

12 M. Garnier, K. Breuer, D. Purdie, M. Hensberger, Y. Baer, and B. Delley, Phys. Rev. Lett. 78, 4127 (1997).

13 S.-H. Yang, H. Kumigashira, T. Yokoya, A. Chainani, T. Takahashi, H. Takeya, and K. Kadowaki, Phys. Rev. B 53, R11946 (1996).

14 H.-D. Kim, O. Tjernberg, G. Chiaia, H. Kumigashira, T. Takahashi, L. Duó, O. Sakai, M.
Kasaya, and I. Lindau, Phys. Rev. B56, 1620 (1997).

15 L. Duo, Surf. Sci. Rept. 32, 233 (1998).

16 M.P. Seah, and W. A. Dench, Surf. Interface Anal. 1, 2 (1979).

17 C.D. Wagner, L.E. Davis, and M. Riggs, Surf. Interface Anal. 2, 53 (1980).

18 Y. Saitoh, H. Kimura, Y. Suzuki, T. Nakatani, T. Matsushita, T. Muro, T. Miyahara, M. Fujisawa, K. Soda, S. Ueda, H. Harada, M. Kotsugi, A. Sekiyama, and S. Suga, Rev. Sci. Instrum. 71, 3254 (2000).

19 C. Laubschat, E. Weschke, C. Holtz, M. Domke, O. Strebel, and G. Kaindl, Phys. Rev. Lett. 65, 1639 (1990).

20 A. Sekiyama, T. Iwasaki, K. Matsuda, Y. Saitoh, Y. Onuki, and S. Suga, Nature, 403, 396 (2000).

21 S.-H. Yang, S.-J. Oh, H.-D. Kim, R.-J. Jung, A. Sekiyama, T. Iwasaki, S. Suga, Y. Saitoh, E.-J. Cho, J.-G. Park, Phys. Rev. B61, R13329 (2000).

22 R.-J. Jung, H.-D. Kim, B.-H. Choi, S.-J. Oh, E.-J. Cho, T. Iwasaki, A. Sekiyama, S. Imada, S. Suga, J.-G. Park, J. Electron Spectro. Rel. Phenomena, 114-116, 693 (2001).

23 R.-J. Jung, B.-H. Choi, J.-H. Kim, J.-G. Chung, S.-J. Oh, E.-J. Cho, T. Muro, A. Sekiyama, S. Imada, S. Suga, J.-G. Park, Y.S. Kwon, (unpublished).

24 B.-H. Choi, R.-J. Jung, H.-D. Kim, S.-J. Oh, E.-J. Cho, T. Iwasaki, Y. Saitoh, A. Sekiyama, S. Imada, S. Suga, J.-G. Park, Y.S. Kwon, (unpublished).

25 J.C. Fuggle, F.U. Hillebrecht, J.-M. Esteva, R.C. Karnatak, O. Gunnarsson, and K. Schonhammer, Phys. Rev. B27, 4637 (1983).

26 T. Jo, and A. Kotani, Phys. Rev. B38, 830 (1988).
Figure Captions

Fig. 1: x-ray absorption spectra of $3d \rightarrow 4f$ transition region for $\text{CeFe}_2$, $\text{CeNi}_2$, and $\text{CeSi}_2$. The symbols marked on the spectrum represent photon energies used for RPES shown in subsequent figures. The bar diagram at the bottom is the theoretical calculation result for the multiplet structure of $3d f^2$ intermediate state taken from ref. [26].

Fig. 2: Ce $f$ spectral weights near the Fermi level for $\text{CeFe}_2$ obtained with various incident photon energies.

Fig. 3: Difference spectra between the $4f$ spectral weights at various photon energies and that at $h\nu = 881.76\text{eV}$.

Fig. 4: Ce $4f$ spectral weights near the Fermi level for $\text{CeNi}_2$ obtained at different photon energies. Shown in the bottom is the difference spectrum between the two.

Fig. 5: Ce $4f$ spectral weight near the fermi level for $\text{CeSi}_2$ obtained at various photon energies. In the bottom the difference spectra are shown.