CORE LEVEL PHOTOEMISSION IN SOLIDS
A. Kotani

To cite this version:

HAL Id: jpa-00227268
https://hal.archives-ouvertes.fr/jpa-00227268
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
CORE LEVEL PHOTOEMISSION IN SOLIDS

A. KOTANI

Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

Abstract - Many body effects in core level photoemission are discussed for rare earth systems, especially for La and Ce compounds both in metallic and insulating forms. The 3d core photoemission spectrum of these materials is analyzed by using the impurity Anderson model incorporated with a core hole potential to the 4f state. Important informations on the metallic mixed valency, as well as on the insulating covalency, are derived from the analysis. The relationship of spectra between the 3d core photoemission and the 2p core photoabsorption is discussed.

I - INTRODUCTION

In the final state of core level photoemission, a core hole is left behind. Within the Hartree-Fock approximation, the Koopmans theorem holds, so that the core level photoemission spectrum is described by discrete lines whose binding energy corresponds to the Hartree-Fock energy eigenvalue $E_{C}$ of core electrons. Historically, the core level photoemission in solids has been developed from the experimental determination of $E_{C}$ in various systems. Since the value of $E_{C}$ in solids is not very different from the corresponding free atom value, which is characteristic in each element, the core level photoemission is useful as a tool of elementary analysis. Furthermore, a small deviation of $E_{C}$ from its free atom value, i.e. the chemical shift, provides us with the information on the chemical bonding of outer electrons.

However, the Koopmans theorem does not generally hold because of the many body effect beyond the Hartree-Fock approximation. When a core hole is created in the final state of photoemission, outer electrons (i.e. valence electrons) are polarized by the core hole potential and screen the core hole charge. This corresponds to the redistribution or relaxation of outer electron states, and the dynamics of many body response of outer electrons to the core hole are sensitively reflected in the structure of photoemission spectrum. Owing to the recent progress in experimental technique, the many body effect in the photoemission spectrum can be observed with sufficient accuracy as an asymmetry of spectral shape and as a satellite structure. Furthermore, it has been well recognized that the core level photoemission is one of the most powerful tools in the study of many body effects of outer electrons /1/.

A well-known example, which demonstrates the importance of the many body effect of outer electrons, is the singularity in core level photoemission spectrum of simple metals. In the final state of core photoemission in simple metals, conduction electrons screen the core hole charge, and this many body response of conduction electrons gives rise to an asymmetric photoemission line shape diverging at the
threshold, due to the so-called orthogonality catastrophe /2,3/. More interesting is the recent development in the study of many body effects in magnetic materials, which contain incompletely filled d or f electrons /1/. The relaxation of d or f electron orbital on the core hole site causes the splitting of core photoemission spectrum, and we can obtain very important information on the d or f electron state from the analysis of photoemission spectrum. In the present paper, we review the development in theoretical study of core level photoemission of rare earth compounds, especially La and Ce compounds both in metallic and insulating forms.

II - La and Ce METALS AND THEIR INTERMETALLIC COMPOUNDS

In the 3d core photoemission spectrum (3d-XPS) of La metal /4,5/, as shown in the inset of Fig. 1 /5/, a weak satellite peak is observed on the lower binding energy side of the main peak. The energy separation between the satellite and the main peak is about 3.4 eV. The intensity of the satellite becomes very large in some intermetallic La compounds, for instance in LaPd /5/. The mechanism of this satellite was first pointed out by Toyozawa and the present author more than ten years ago /6,7,8/. As a model simulating the La metal, let us consider a system which consists of a conduction band, well-localized 4f states and core states, as shown in Fig. 1. We take account of a hybridization V between 4f and conduction electrons. In the initial state of photoemission, the 4f level E<sub>f0</sub> is well above the Fermi level E<sub>F</sub>, so that we have no 4f electron occupied in the 4f level, corresponding to the 4f<sub>0</sub> ground state of La. However, in the final state of photoemission, the 4f level on the core hole site is pulled down below E<sub>F</sub> due to the attractive potential of the core hole. Then, we expect to have two classes of final states, corresponding to two different configurations of 4f state. In one class, a conduction electron near E<sub>F</sub> jumps into the 4f level through the hybridization V (see Fig. 1), while in the other class, the 4f level is still empty even after being pulled down below E<sub>F</sub>. The former (4f<sup>0</sup> configuration) gives rise to the satellite peak of the photoemission spectrum, while the latter (4f<sup>0</sup> configuration) the main peak. In the former, the core hole charge is screened by the 4f electron, so this final state is called the well-screened state, while the latter final state is denoted by the poorly-screened state. In LaPd<sub>3</sub>, the intensity of the satellite becomes larger, since the effect of hybridization V becomes larger due to the existence of Pd 4d conduction band.

A very similar satellite structure is also observed in the system containing trivalent Ce /5,9/, such as γ-Ce and CeAl<sub>2</sub>, and it can be explained by essentially the same mechanism as above. In the trivalent Ce, one 4f electron is already occupied in the

![Fig. 1 - Model of our system describing the core photoemission process in La metal. Experimental data of 3d-XPS in La and LaPd<sub>3</sub> are shown in the inset.](image-url)
ground state because $\varepsilon_f^0$ is well below $\varepsilon_F$, but one more 4f electron can be transferred from the conduction band in the final state of photoemission. Therefore, the satellite comes from the 4f$^2$ well-screened final state, while the main line from the 4f$^1$ poorly-screened final state.

III - MIXED VALENCE Ce COMPOUNDS

The 3d-XPS of mixed valence Ce compounds exhibits three-peak structure (apart from the spin orbit splitting). As an example, the 3d-XPS of CePd$_3$ is shown in the inset of Fig. 2/5/. In the ground state of mixed valence systems, the 4f level $\varepsilon_f^0$ is located close to the Fermi level $\varepsilon_F$, so that the 4f state hybridizes with the conduction band, and the ground state is a quantum-mechanically mixed state between 4f$^0$ and 4f$^1$ configurations. The occurrence of three peaks in 3d-XPS is understood, at least qualitatively, from the mechanism of the satellite in La and trivalent Ce: When we take account of the 4f$^1$ component of the mixed valence ground state, we expect to have well-screened 4f$^1$ and poorly-screened 4f$^1$ final states, as in the case of La. But, when we take account of the 4f$^0$ component, we expect to have well-screened 4f$^0$ and poorly-screened 4f$^0$ final states, as in the case of trivalent Ce. Therefore, combining the two cases, we expect to have three different configurations, 4f$^0$, 4f$^1$ and 4f$^2$, in the final state, and they give rise to the three peaks in 3d-XPS.

As found from the above mechanism, the structure of 3d-XPS depends sensitively on the hybridization between 4f and conduction electrons both in the initial and final state of photoemission. This means that we can obtain important information on the 4f electron state by analyzing quantitatively 3d-XPS data. Such a quantitative theoretical analysis was first made by Gunnarsson and Schönhammer/10/ with the use of the impurity Anderson model. The following argument in this section is based mainly on their theory, with some minor modification. To make the model explicit, we describe the Hamiltonian for 4f and conduction electrons. The Hamiltonian is given by

$$ H_0 = \sum_k \varepsilon_k a_k^+ a_k + \varepsilon_f^0 a_f^+ a_f + U_{fF} \sum_{kV} a_f^+ a_k^+ a_{kV} a_{fV} + \frac{V}{N} \sum_{kV} (a_k^+ a_{fV} + a_{fV} a_k) \tag{1} $$

in the initial state of photoemission, while it is changed into

$$ H = H_0 - U_{fC} \sum_{kV} a_{kV} a_{fV} \tag{2} $$

in the final state. Here, $\varepsilon_k$ and $\varepsilon_f^0$ are energies of the conduction band and 4f

![Fig. 2 - Theoretical and experimental (inset) results of the 3d-XPS of CePd$_3$.](image)
level, respectively, and $a_{+}^{\dagger}$ and $a_{-}^{\dagger}$ are electron creation operators in these states, where the index $k$ denotes the energy level of conduction electrons ($k = 1 \sim N$) and $\nu$ specifies both the spin and orbital degeneracy ($\nu = 1 \sim N_{\nu}$). Interactions $V$, $U_{eff}$ and $-U_{f}$ represent, respectively, the hybridization between 4f and conduction band states, the Coulomb interaction between 4f electrons and the core hole potential. It is convenient to calculate the photoemission spectrum by using the $1/N_{f}$ expansion method ($N_{f}$ being the degeneracy of 4f level). In diagonalizing the Hamiltonian $H_{0}$ or $H$, it is noted that the coupling among the states $A$, $B$ and $C$ of Fig. 3 occurs within the lowest order of $1/N_{f}$, but the coupling of these states with the other ones, $D$, $E$, $F$, etc., occurs only as a higher order correction with respect to $1/N_{f}$. Since the value $N_{f}$ is large (we usually take $N_{f} = 14$), the lowest order approximation provides us with sufficiently reliable results. Once we diagonalize $H_{0}$ and $H$, the core photoemission spectrum is calculated by

$$F_{XPS}(E_{g}) = \frac{1}{\pi} \frac{\Gamma/\pi}{(E_{B}-E_{g}+E_{B})^{2}+\Gamma^{2}}$$

where $|g>$ is the ground state of $H_{0}$ with energy $E_{g}$, $|f>$'s are eigenstates of $H$ with energies $E_{f}$'s, $E_{B}$ is the binding energy, and $\Gamma$ represents the spectral broadening due to the lifetime of the core hole, as well as the experimental resolution. In Fig. 2, we show 3d-XPS of CePd$_{2}$ calculated within the lowest order approximation of $1/N_{f}$ expansion /11/. In order to reproduce the experimental 3d-XPS, we used the following parameter values: $V = 0.38$, $U_{eff} = 8.3$, $U_{f} = 10.5$, $E_{F}^{0} - E_{F} = -2.0$ and $\Gamma = 1.6$ in units of eV. With these parameters, the average 4f electron number $n_{f}$ in the ground state is estimated as $n_{f} = 0.86$.

Gunnarsson and Schönhammer /5,10/ performed systematic analysis of 3d-XPS in various Ce compounds, and revealed that the intermetallic Ce compounds with Ni, Co, Ru etc. are in the mixed valence state (with fractional value of $n_{f}$), although these compounds were traditionally considered to be in the tetravalent state (with $n_{f} = 0$).

IV - INSULATING Ce COMPOUNDS

Much interest has recently been taken in the insulating Ce compounds CeO$_{2}$. CeO$_{2}$ was traditionally considered to be tetravalent, but the 3d-XPS of CeO$_{2}$ exhibits three-
peak structure /12,13,14/, as shown in the inset of Fig. 4 /14/, somewhat similarly to that of mixed valence Ce intermetallics. Even in insulating Ce compounds, it can be shown that if the 4f level $e_{F}^{0}$ is located close to the filled valence band the ground state is described by a mixture between $4f^{0}$ and $4f^{1}$ configurations /14,15,16,17/. We can use Hamiltonians (1) and (2) only by regarding $e_{k}$ as the filled valence band of oxygen 2p states. In this case, $V$ represents the covalency mixing between 4f and valence band states. Therefore, if the ground state contains both of $4f^{0}$ and $4f^{1}$ configurations, it is possible to have three different final configurations, $4f^{0}$, $4f^{1}$, and $4f^{2}$, because a charge transfer can occur from the valence band to the 4f state in the final state. We show the calculated 3d-XPS of CeO$_{2}$ in Fig. 4 /11/, where the parameter values are taken as $V = 0.76$, $U_{eF} = 10.5$, $U_{FC} = 12.4$, $e_{F}^{0} - e_{v}^{0} = 1.6$ and $\Gamma = 1.0$ in units of eV /11,17/ ($e_{0}$ being the center of the valence band). In this calculation Hamiltonians (1) and (2) are diagonalized numerically for a finite system where $e_{k}$ is taken as

$$e_{k} = e_{v}^{0} - \frac{W}{2} + \frac{W}{N} (k - \frac{1}{2})$$

with $k = 1, 2, \ldots N$. The band width $W$ is chosen as 3.0 eV, and the value of $N$ is taken to be sufficiently large so that the calculated spectrum converges well. From this calculation the average 4f electron number in the ground state of CeO$_{2}$ is found to be about 0.5, so that 4f$^{0}$ and 4f$^{1}$ configurations are found to be mixed very strongly.

Very recently, experimental observation of 3d-XPS has been made for another "nominally tetravalent" insulating Ce compound CeF$_{4}$ /18/. As shown in the inset of Fig. 5, the 3d-XPS of CeF$_{4}$ has three peaks, whose energy spacings and relative intensities are somewhat different from those of CeO$_{2}$. Theoretical analysis of this spectrum is also made by using the same model as CeO$_{2}$ and by somewhat modifying the parameter values /19/. The result is shown in Fig. 5, where we used the parameters of $V = 0.76$, $U_{eF} = 8.5$, $U_{FC} = 12.0$, $e_{F}^{0} - e_{v}^{0} = 4.0$, $W = 3.0$ and $\Gamma = 1.0$ in units of eV. The background spectrum $B(E_{B})$ is also taken into account, as plotted with the dashed curve, where it is assumed to be given by

$$B(E_{B}) = C \int_{E_{B}}^{E_{B}^{\text{up}}} F_{\text{XPS}}(E_{B}) dE_{B}$$

with a constant $C$ as an adjustable parameter. The agreement between the calculated and observed spectra is satisfactory.

The most essential difference in the estimated parameter values between CeF$_{4}$ and CeO$_{2}$ is that the value of $e_{F}^{0} - e_{v}^{0}$ in CeF$_{4}$ is much larger than that in CeO$_{2}$, corresponding to larger electronegativity of the fluorine ion. Compared with the
case of CeO₂, therefore, the hybridization between 4f and valence band states in the ground state of CeF₄ becomes smaller, and the average 4f electron number $n_\text{f}$ is estimated to be about 0.29, which is considerably smaller than that of CeO₂. Of the three peaks of 3d-XPS both in CeF₄ and CeO₂, the highest binding energy peak corresponds mainly to the 4f⁰ final state, while the middle and the lowest binding energy peaks are mixed states between 4f¹ and 4f² final states. The fractional intensity of the highest binding energy peak is larger in CeF₄ than in CeO₂, which is caused by the larger weight of the 4f⁰ configuration in the ground state.

In this way, the core photoemission gives the information on the covalency mixing between different 4f configurations in insulating compounds. The mechanism of the satellite is essentially the same between insulating and metallic systems. The characteristic feature in metallic systems is the existence of electron hole pair excitations in the conduction band, as shown in D, E, F, etc. in Fig. 3, in contrast that they are absent in insulating systems. However, the contribution of these states with electron hole pairs (D, E, F, etc.) to the photoemission spectra is much smaller than those with no electron hole pair (A, B, C), as mentioned before. Therefore, when we regard the filled valence band in insulating systems as the conduction band below $E_F$ in metallic systems, the formal theoretical procedure in calculating 3d-XPS is essentially the same between insulating and metallic systems. The difference in the spectral features in different systems comes only from the difference in the parameter values included in the model system. In this sense, we can say that CeO₂ and CeF₄ are also in the "mixed valence" state, and we cannot distinguish between the metallic mixed valency and the insulating covalency from core photoemission data.

![Fig. 5 - Theoretical and experimental (inset) results of the 3d-XPS of CeF₄.](image)

V - RELATION BETWEEN 3d-XPS AND L₃-XAS

In the 2p core photoabsorption (L₃-XAS) of Ce compounds, a 2p electron is excited to the Ce 5d conduction band, as shown in Fig. 6 for the case of insulating Ce compounds. Therefore, we have a core hole left behind in the final state, and the core hole potential $-U_{\text{f}}$ is expected to cause the final state interaction very similar to that of 3d-XPS. According to experimental data, however, characteristic features of L₃-XAS in various Ce compounds are usually different from those of 3d-XPS. The difference between 3d-XPS and L₃-XAS is observed most clearly in insulating Ce compounds CeO₂ and CeF₄. The 3d-XPS of these systems has three peaks, as shown before, whereas the L₃-XAS has only two peaks /13,18,20,21,22/. Experimental data of L₃-XAS in CeF₄ is shown in the inset of Fig. 7 /18/. The energy separation of two peaks in L₃-XAS is about 6 eV in CeF₄ and about 8 eV in CeO₂, whereas the energy
separation of the outermost peaks in 3d-XPS is about 14 eV in CeF and about 16 eV in CeO₂ (see insets of Figs. 4 and 5). This result suggests that 4f configurations in final states of 3d-XPS and L₃-XAS are different. As an origin of this difference, two possible mechanisms can be considered: (i) A difference in the core hole potential \(-U_{dc}\) between 2p and 3d core holes. (ii) The existence of a photoexcited 5d electron in the final state of L₃-XAS.

Jo and the present author /11,23/ considered that the point (ii) is essentially important, and proposed a mechanism by which the 3d-XPS and L₃-XAS in CeO₂ are explained consistently. A similar calculation has also been made for CeF /197. In these calculations, the interaction \(U_{5d}\) between the photoexcited 5d electron and the 4f electron, as well as the attractive potential \(-U_{dc}\) of the core hole acting on the 5d electron, are taken into account, as shown in Fig. 6. On the other hand, it is assumed that the core hole potential \(-U_{dc}\) acting on the 4f electron is the same for the 3d and 2p core holes, with disregarding the possibility (i). The role of the potential \(-U_{dc}\) is to localize the 5d electron near the core hole site, and then due to the interaction \(U_{5d}\) the 4f electron configurations in the final state of L₃-XAS become different from those of 3d-XPS. As an example, we show in Fig. 7 /197 the result of L₃-XAS of CeF, which is calculated by using the parameter values determined from the analysis of 3d-XPS and by assuming the 5d band width of 6.0 eV and \(\Gamma = 2.5\) eV. The values of \(U_{5d}\) and \(U_{dc}\) are changed as parameters. It is found that when we use \(U_{5d} = 4.0\) eV and \(U_{dc} = 5.0\) eV the calculated L₃-XAS (the solid curve) is in good agreement with the experimental result both in the energy separation and the relative intensity of two peaks (by taking account of the background as shown with the dashed curve in the inset of Fig. 7). On the other hand, when we disregard the effect of \(U_{5d}\) and \(U_{dc}\), as shown by the dashed curve, the L₃-XAS is a simple convolution of 5d-XPS with the density of states of 5d band, and the obtained spectrum is quite different from the experimental result. The importance of \(U_{5d}\) and \(-U_{dc}\) was also confirmed in the analysis of L₃-XAS in CeO₂ /11,22,23/ and in insulating La compounds, La₂O₃ and LaF₃ /24/.

On the possibility of (i), a theoretical calculation by Herbst and Wilkins /25/ indicates that \(U_{5d}\) of 3d core hole in Ce metal is larger than that of the 2p core hole by 1.3 eV, but no calculation has been made for insulating systems. According to recent 3p core spectroscopies in CeO₂, it is confirmed that the point (i) is less

Fig. 6 - Model of L₃-XAS in CeF₄.

Fig. 7 - Theoretical and experimental (inset) results of the L₃-XAS of CeF₄.
important than (ii). The 3p-XAS of CeO$_2$ observed by Kaindl et al. /26/ is very similar to L$_3$-XAS, although the spectral width is larger. Furthermore, the 3p-XPS, which has very recently been observed by Bianconi et al. /27/, can also be reproduced fairly well from the 3d-XPS by increasing the spectral width and by adding a background contribution. Therefore, we can conclude that the value of $U_{fc}$ is almost the same for 2p, 3p, and 3d core holes. The difference in the experimental spectra between 3p-XAS and 3p-XPS can be explained only by the effect of $U_e$ and $-U_{dc}$. Although there remains a possibility of the difference in $U_{fc}$ between 3p and 3d (or 2p) core holes by about 1 eV due to the experimental uncertainty, the 1 eV difference in $U_{fc}$ is too small to explain the difference between 3d(or 3p)-XPS and 2p(or 3p)-XAS.

In mixed valence Ce intermetallics, L$_3$-XAS has also two peaks /13,20,21/, but the difference between 3d-XPS and L$_3$-XAS is not so remarkable as that in CeO$_2$ and CeF$_4$. A preliminary analysis of L$_3$-XAS in CePd$_3$ /11,28/ suggests the importance of the effect of $U_e$ and $-U_{dc}$, but the values of $U_{fc}$ seem to be much smaller than those of insulating Ce compounds. More detailed investigations will be needed in analyzing L$_3$-XAS of metallic mixed valence compounds.

VI - CONCLUDING REMARKS

We have discussed many body effects in core level photoemission in solids containing incompletely filled 4f states. It is shown that the analysis of 3d-XPS with the impurity Anderson model provides us with important information on the 4f state. In addition to the materials treated in this paper, theoretical and/or experimental studies have been made for CeO$_2$, PrO$_2$, TbO$_2$, and so on /29,30/. It is to be mentioned that the impurity Anderson model has also been used successfully in the analysis of core level photoemission of transition metal compounds /31/.

The author would like to express his thanks to Prof. T. Jo, Prof. A. Bianconi, Dr. J.C. Parlebas, Dr. A. Marcelli, Dr. K. Okada, Dr. T. Nakano, and Mr. M. Okada for valuable discussion and fruitful collaboration. This work is partly supported by The Kurata Research Grant, the France-Japan Collaboration Project on Magnetism, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan.

REFERENCES