

Lifetime effect on the multiplet structure of $4d$ x-ray-photoemission spectra in heavy rare-earth elements

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(Received 28 March 1994)

X-ray-photoemission spectra of $4d$ ($N_{4,5}$) core level in heavy rare-earth elements are studied theoretically with the consideration of the $4d-4f4f$ ($N_{4,5}-N_{6,7}N_{6,7}$) super-Coster-Kronig decay process in the excited states. It is shown that the lifetime broadening of the states in the multiplets strongly varies with their binding energies. The calculation considering the decay effect reproduces the experimental spectrum fairly well. The generally adopted assumption of the constant core-hole lifetime broadening breaks down completely if the coupling between a core-hole and unfilled valence shell is strong and yet the decay process is dominated by the coupling between them. The tendency in the lifetime broadening, that the larger binding energy states have the wider width, can be understood from a point of view of electron correlation.

I. INTRODUCTION

In x-ray-photoemission spectra (XPS) one expects peaks which correspond to the Hartree-Fock (HF) energy of the one-electron orbit according to Koopmans' theorem. In many cases rather narrow and sharp peaks are really observed in the energy position where they are expected. This shows that the concept of one-electron orbit is valid and that the neglect of relaxation in the final state is good as a first approximation. There are, however, not a few cases in which one has to proceed beyond this simple approximation even for a qualitative understanding.

The XPS can be related to a Green's function. Spectral peaks appear in the position of the poles of the Green's function. If relaxation in the final state is ignored, the δ -function-like peaks appear in the one-electron orbital energy just as Koopmans' theorem states. When relaxation is introduced, those peaks would be shifted and broadened. These effects can be expressed by the self-energy, which changes the position of the poles. The shifts are related to the real part of the self-energy, and the broadening to the imaginary part. The fact that the experimental core XPS line is generally sharp indicates the stability of core holes. This justifies the concept of one-electron orbit and lifetime of a core hole.

When an atom has an unfilled valence shell, XPS sometimes shows complex multiplet structure. The multiplet structure is caused by the electrostatic interaction between a core hole and the unfilled shell or within the unfilled shell. Multiplet coupling can be thought of as the first-order perturbation that splits the degenerate term averaged HF energy. It is believed that the concept of lifetime of a core hole is still valid and constant over the multiplets.

In this paper we will treat the $4d$ -XPS in heavy rare-earth elements, which have unfilled $4f$ valence shells.

The electrostatic interaction between the $4d$ and $4f$ shell is very large because they have the same principal quantum number. The wide spread multiplet structure in rare-earth $4d$ -XPS was measured experimentally in the 1970's for metals and compounds.¹⁻⁶ Orchard and Thornton measured the $4d$ -XPS of rare-earth sesquioxides (R_2O_3) and compared some of them with their calculation for a simple ionic model.⁶ The agreement was not very good. In the cases of light rare-earth elements, the experimental spectra show satellite structure which is not present in their theory. They pointed out that these satellites might be due to the charge-transfer effect. In the case of heavy rare-earth elements, the theoretical results show stronger and sharper structure in the high-binding-energy region than experiment.

It was shown afterward that, for the light rare-earth elements, theoretical calculations including both the multiplet and charge-transfer effect with an impurity Anderson model reproduces the experimental spectra very well.⁷ For the heavy rare-earth elements, however, it was found from the analysis of the $3d$ -XPS,⁸ that the charge-transfer effect is negligible and the ionic model should be applied for them. There were suggestions that the large super-Coster-Kronig (s-CK) decay may broaden and distort the spectra,^{2,6} although there remains a question why the edge structure in the lowest binding-energy region is observed quite sharply.

The lifetimes of core holes were discussed by several authors. Among them McGuire's theoretical calculations are most well known. Fuggle and Alvarado⁹ made the comparison between experiments and theory. They found a large discrepancy between experiments and McGuire's theory for the $N_{4,5}$ shell.¹⁰ Afterwards Ohno and Wendin¹¹ discussed the N -shell linewidth with more sophisticated theory and got a reasonable agreement with experiment. However the rare-earth elements are not treated in these works, maybe because of the multiplet

structure.

The aim of this paper is to discuss the $4d$ -XPS in heavy rare-earth elements by an ionic model with the explicit consideration of decay effect in the final state. It is shown that the experimental spectra can be reproduced fairly well with this model, and that the lifetime broadening varies strongly within a multiplet. It is essential to take into account the multiplet term-dependent decay effect for the $4d$ -XPS in heavy rare-earth elements.

In Sec. II, we will give the formulation for our model. In Sec. III, we will give the calculated spectra and make a comparison with experimental data for metals and oxides. In Sec. IV, we will discuss our results and explain the multiplet term dependence of the lifetime. In Sec. V, we will make concluding remarks and summarize the problems left.

II. FORMULATION

In the sudden approximation, the photoemission intensity is given by

$$I(E_B) = \sum_f |\langle f | a_{\text{core}} | g \rangle|^2 L(E_B + E_g - E_f), \quad (1)$$

where a_{core} is the annihilation operator of a core electron, the ground and final states (energies) are described by $|g\rangle, (E_g)$ and $|f\rangle, (E_f)$, respectively, and E_B is the binding energy. $L(E)$ is a function which represents the energy conservation condition. It is usually written as a delta function $\delta(E)$ (line spectrum) or Lorentzian function $\Gamma / [\pi(E^2 + \Gamma^2)]$ [broadened by Γ , half width at half maximum (HWHM)].

The function $L(E)$ is related to the final-state Green's function by

$$L(E) = \frac{1}{\pi} \text{Im} G_f(E), \quad (2)$$

where the $\text{Im} G_f$ is the imaginary part of Green's function for the final states. If the final states are the real eigenstates, the above $L(E)$ becomes a δ function. If the final states have only a limited lifetime τ , the energy conservation δ function becomes Lorentzian function with Γ (HWHM) = \hbar/τ because of the uncertainty principle. We will discuss the effect of decay processes in the final states explicitly by the above equation in the following.

The final-state Green's function is written

$$G_f(E) = \left\langle f \left| \frac{1}{z - H_f} \right| f \right\rangle [z = E - i\eta (\eta \rightarrow 0)] \quad (3)$$

$$= \left\langle f \left| \frac{1}{z - H_0 - H_1} \right| f \right\rangle \quad (4)$$

$$= \frac{1}{z - E_f^0 - \Sigma_f(z)} \quad (5)$$

$$= \frac{1}{z - E_f^0 - \text{Re}\Sigma_f(z) - i\text{Im}\Sigma_f(z)}, \quad (6)$$

where $H_f = H_0 + H_1$ is the Hamiltonian in the final state, H_0 is the HF central field plus multiplet splitting part of

H_f and E_f^0 is its eigenvalue. H_1 represents configuration interaction (CI). The function $\Sigma_f(E)$ is the self-energy in which H_1 is regarded as perturbation. The off-diagonal part of Green's function was ignored for simplicity. We can see that the position of the poles is shifted and becomes complex.

From Eq. (6), the $L(E)$ in Eq. (2) can be expressed as

$$L(E) = \frac{1}{\pi} \frac{\text{Im}\Sigma_f(E)}{[E - E_f^0 - \text{Re}\Sigma_f(E)]^2 + [\text{Im}\Sigma_f(E)]^2}. \quad (7)$$

The energy of a pole is given by solving the equation

$$E = E_f^0 + \text{Re}\Sigma_f(E). \quad (8)$$

If we have found the correct energy E_f of a particular pole, we can approximate Eq. (7) to a Lorentzian form near the pole. This is accomplished by Taylor expansion of the self-energy around E_f

$$E - E_f^0 - \text{Re}\Sigma_f(E) \simeq Z_f(E_f)^{-1} (E - E_f), \quad (9)$$

$$Z_f(E) = \left[1 - \frac{\partial}{\partial E} \text{Re}\Sigma_f(E) \right]^{-1}. \quad (10)$$

Then Eq. (7) becomes

$$L(E) \simeq \frac{Z_f(E_f)}{\pi} \frac{\Gamma_f}{(E - E_f)^2 + \Gamma_f^2}, \quad (11)$$

where

$$\Gamma_f = Z_f(E_f) \text{Im}\Sigma_f(E_f). \quad (12)$$

We can now see that the energies of the multiplets are shifted by $\text{Re}\Sigma_f(E_f)$ and have broadened by Γ_f (HWHM).

The calculation of the self-energy is rather complicated and cumbersome. It is well known that the multiplet splitting width is reduced to about 80% of the HF value even for the ground configuration and that this reduction is caused by a little admixture of many excited configurations. Here, we decide to take the self-energy shift (real part effect of the self-energy) into account by just reducing the Slater integrals to fit the experiment, and do not estimate the value explicitly.

We only calculate the imaginary part of the self-energy. The self-energy to the lowest order is obtained as

$$\Sigma_f(E) = \sum_A \frac{|\langle A | H_1 | f \rangle|^2}{E - E_A}, \quad (13)$$

where $|A\rangle$ and E_A , respectively, represent the decayed states and their energies.

Now Eqs. (11) and (12) become

$$L(E) \simeq \frac{1}{\pi} \frac{\Gamma_f}{(E - E_f)^2 + \Gamma_f^2} \quad (14)$$

and

$$\Gamma_f = \text{Im}\Sigma_f(E_f), \quad (15)$$

where we approximated $Z_f(E_f)$ to be unity. From Eq. (13) the lifetime broadening Γ can be written as

$$\Gamma_f = \pi \sum_A |\langle A | H_1 | f \rangle|^2 \delta(E_A - E_f). \quad (16)$$

We only consider the $4d-4f4f$ s-CK decay channel in the calculation, because it is the dominant process, and might be enough to estimate the *imaginary part* of the self-energy. Then the configurations of the states $|A\rangle$ and $|f\rangle$ in Eq. (16) represent $4d^{10}4f^{n-2}\epsilon l (l=s,d,g,i,l)$ and $4d^9 4f^n$, respectively.

In the next section we will calculate the $4d$ -XPS, according to Eqs. (1) and (14). The calculated line spectra will be convoluted by Lorentzian with a width obtained from Eq. (16) for each multiplet state.

III. CALCULATION

In this section we calculate the $4d$ -XPS in heavy rare-earth ($R = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) metals and sesquioxides. Rare-earth atoms are trivalent in those materials except for Eu and Yb, which are divalent in the metal and trivalent or slightly mixed valent in the sesquioxide. We employ the trivalent ionic model for the calculation.

The Slater integrals and spin-orbit coupling constants are calculated by the Hartree-Fock method with relativistic corrections.¹² The symmetry of the Auger electron was taken to be g , because the Slater integrals of the others were negligibly small. The wave function of the continuum electron was calculated from the self-consistent one-electron potential without the continuum electron. The kinetic energy of the continuum electron was decided such as to keep the total average energy of configurations $|f\rangle$ and $|A\rangle$ equal.

The parameter values used are given in Table I. The Slater integrals $F^k(4f4f)$, $F^k(4d4f)$, and $G^k(4d4f)$ are reduced to 80, 75, and 66% of their HF values, respectively.¹³ The Slater integrals for the $4d-4f4f$ (eg) s-CK decay $R^k(4f4f, 4deg)$ are reduced to 80% in order to fit the experiment. For the spin-orbit coupling constants ζ_{4d} and ζ_{4f} the original values are used.

The reduced matrix elements required are calculated by Cowan's program.¹² Hund's ground state is used as the ground-state configuration. Hamiltonians are diagonalized numerically, and the line strength and lifetime

broadening are derived by transforming the transition and s-CK Auger matrices with the eigenvectors.

The calculated results are shown in Figs. 1–10. Panels (c) are the broadening Γ_f of all multiplets including those which have no intensity. In panels (d) we show the results convoluted with constant Lorentzian broadening of 0.7 eV (HWHM). Panels (b) are the results which should be compared with experiments, where the line spectra are convoluted with lifetime broadening by Lorentzian and with instrumental resolution by Gaussian of 0.7 eV (HWHM). The background effects are also included.⁸ Panels (a) are experimental results for metals and oxides. Next we see the results separately for each element.

In Fig. 1 the results for Lu are shown. Lu^{3+} has $4f^{14}$ filled shell in the ground state. The spectrum was split into two components by a $4d$ core spin-orbit interaction. The lifetime widths of both components are the same, because the $4f$ shell is spherical. This can be clearly seen in the experiment for the oxide. The two spin-orbit components have statistical intensity ratio $\frac{2}{3}$ and the same width. The experiment for metal shows extra broad structure which is common to other rare-earth metals. This structure may have its origin in the screening of the conduction band.¹⁴ Yb metal also has $4f^{14}$ configuration. Its spectrum [Fig. 2(a)] is quite similar to Lu metal.

In Fig. 2 we made a calculation for Yb^{3+} ion, although the ground state of Yb_2O_3 seems to be a mixed valent one and has a several percent admixture of divalent component. We can neglect this effect at first approximation. The spectrum shows a wide spread structure over 30 eV, which is due to the strong $4d-4f$ Coulomb-exchange interaction. If we convolute the line spectra with constant Γ [Fig. 2(d)], we expect many peaks over the whole energy region. In the experiment, however, there is only one peak at the edge and there are broad bumps in the higher-binding-energy region. If we convolute the line spectra with the term dependent Γ_f , our calculation reproduces the experiment quite well. It can be seen from Fig. 2(c) that the term in the edge has a width about one half as large as others.

The lifetime effect becomes more drastic as the number of $4f$ electrons decreases. The experiment for Tm ($4f^{12}$) does not show clear structure, while the convolution by

TABLE I. Slater integrals and spin-orbit coupling constants used in the calculation. F , G , and ζ are given in eV, R in $\sqrt{\text{eV}}$.

Z	Lu 71	Yb 70	Tm 69	Er 68	Ho 67	Dy 66	Tb 65	Gd 64	Eu 63	Sm 62
$F^2(4f,4f)$			13.9	13.6	13.4	13.1	12.8	12.4	12.1	11.8
$F^4(4f,4f)$			8.8	8.6	8.4	8.2	8.0	7.9	7.7	7.5
$F^6(4f,4f)$			6.3	6.2	6.1	5.9	5.8	5.7	5.5	5.4
ζ_{4f}		0.39	0.36	0.33	0.30	0.27	0.24	0.22	0.19	0.17
ζ_{4d}	3.9	3.6	3.3	3.1	2.8	2.6	2.4	2.2	2.0	1.8
$F^2(4d,4f)$		14.5	14.3	14.0	13.7	13.4	13.1	12.8	12.5	12.2
$F^4(4d,4f)$		9.3	9.2	9.0	8.8	8.6	8.4	8.2	8.0	7.8
$G^1(4d,4f)$		15.0	14.7	14.4	14.2	13.9	13.6	13.3	13.0	12.7
$G^3(4d,4f)$		9.5	9.3	9.1	8.9	8.8	8.6	8.4	8.2	8.0
$G^5(4d,4f)$		6.7	6.6	6.5	6.3	6.2	6.1	5.9	5.8	5.7
$R^1(4deg,4f^2)$	-0.74	-0.75	-0.74	-0.75	-0.76	-0.77	-0.78	-0.78	-0.79	-0.79
$R^3(4deg,4f^2)$	-0.43	-0.43	-0.43	-0.43	-0.45	-0.46	-0.46	-0.46	-0.47	-0.46
$R^5(4deg,4f^2)$	-0.28	-0.29	-0.29	-0.30	-0.30	-0.31	-0.32	-0.32	-0.32	-0.32

constant Γ has a many-peak structure. Although the edge structure calculated with the term dependent Γ_f is too sharp, good agreement with experiment can be obtained when we convolute this spectrum with a constant

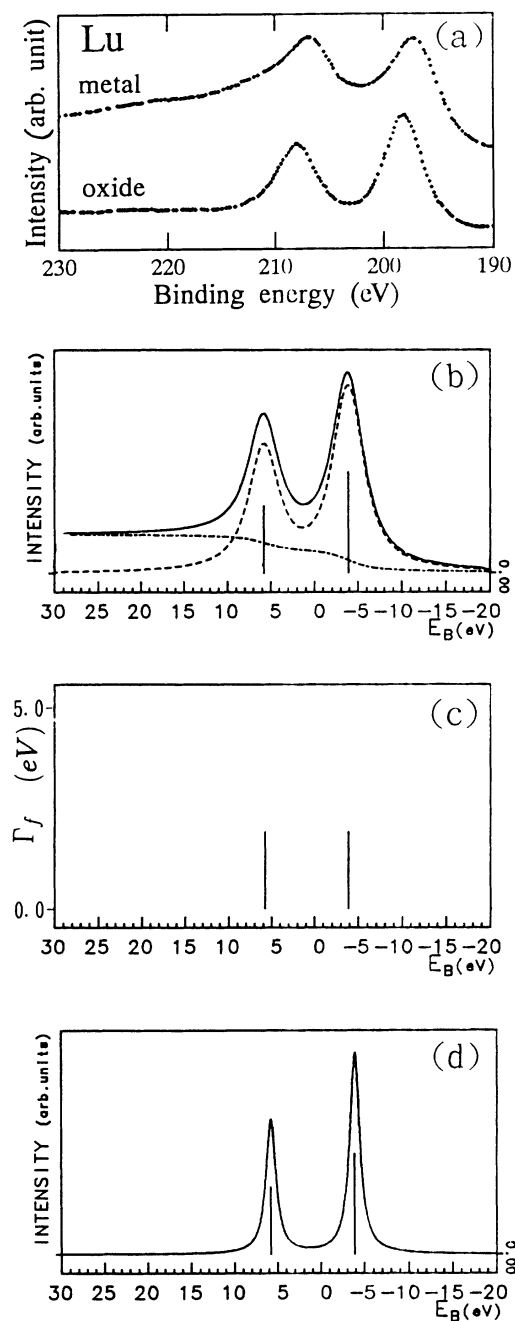


FIG. 1. Experiments and calculation for Lu. (a) Experiments for metal (upper) and oxide (lower) taken from Ref. 4. (b) Calculation considering multiplet dependent lifetime (Γ_f) and instrumental Gaussian [0.7 eV (HWHM)] broadening. Vertical bars are line spectra. Dashed line is the convoluted spectra. Dash-dotted line represents background effect (Ref. 8). Solid line is the sum of dashed and dash-dotted lines. (c) Calculated lifetime broadening Γ_f for all multiplets including those which have no intensity. (d) Calculation with constant Lorentzian [$\Gamma=0.7$ eV (HWHM)] broadening.

width Gaussian, which represents the instrumental resolution.

In Figs. 4 and 5, the results for Er($4f^{11}$) and Ho($4f^{10}$) are shown. The calculation reproduces the experiment very well especially for metal. The oxide spectra can be fitted, if we convolute with larger Gaussian width. We will discuss this point later.

In Figs. 6 and 7 for Dy ($4f^9$) and Tb ($4f^8$), it can be seen that the spectra begin to split into two parts. This

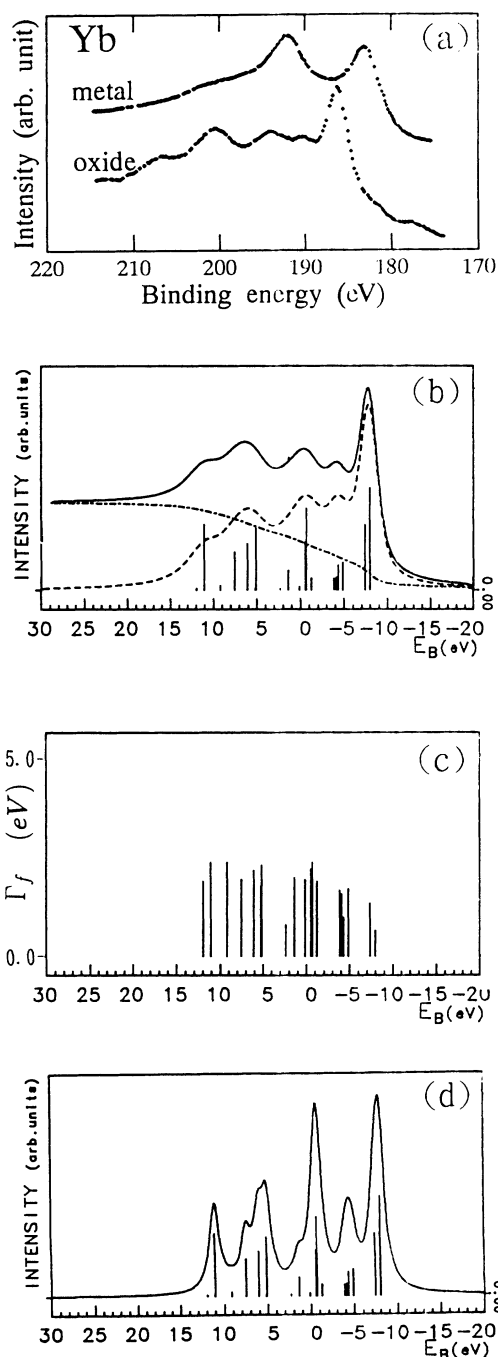


FIG. 2. Experiments and calculation for Yb. Yb metal is divalent.

tendency becomes clear in Gd ($4f^7$) in Fig. 8. The $4f$ shell in a Gd^{3+} ion is in the half-filled state, and its ground state has symmetry of $S=\frac{7}{2}$, $L=0$, $J=\frac{7}{2}$. The two parts in the final state correspond to states with the $4d$ and $4f$ spins parallel and antiparallel.

The main part in the low-binding-energy region is again split into two peaks separated about 5 eV by $4d$ core pin-orbit interaction. Kowalczyk *et al.*³ suggested that this splitting was caused by the exchange interaction

and assigned these peaks as 9D (lower) and 7D (higher). However, the exchange component 7D is located about 30 eV above the main peak.

The lifetime broadening widths of the spin parallel states (9D) are almost zero, while those of spin antiparallel states (7D) are several electron volts [Fig. 8(c)]. The effect of the term-dependent lifetime broadening can now be seen only on the high-binding-energy 7D structure. The sharpness of the 9D states is confirmed by the experi-

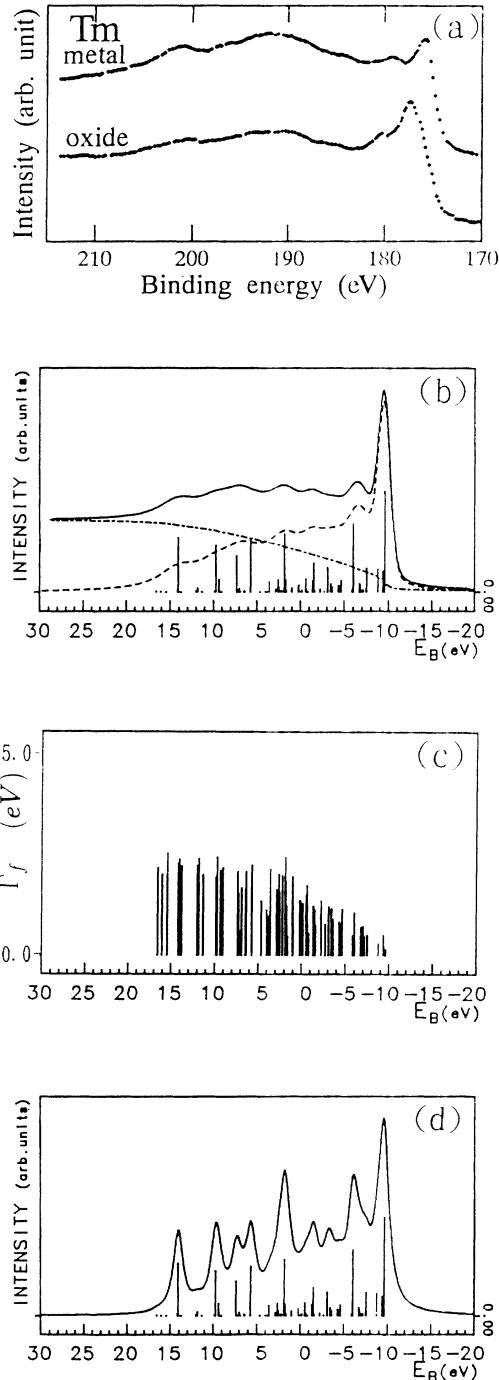


FIG. 3. Experiments and calculation for Tm.

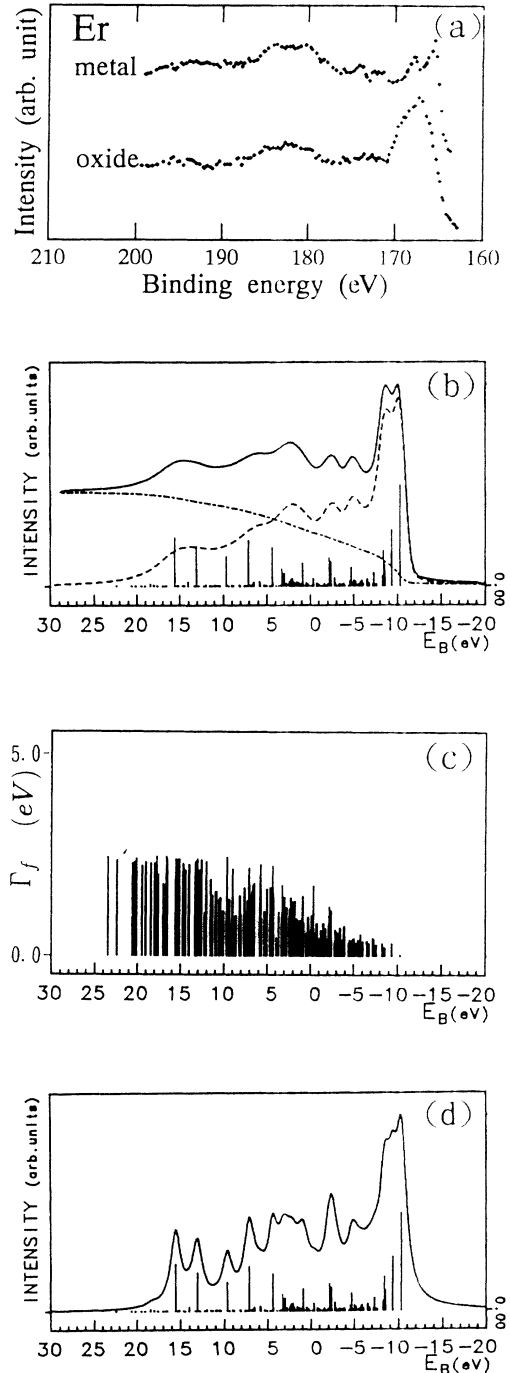


FIG. 4. Experiments and calculation for Er.

ment for Eu metal. In this experiment even the $4f$ spin-orbit manifold in the lowest peak structure (${}^9D_{6,5,4,3,2}$) is resolved.

The same situation holds for lighter elements. As we can see in Figs. 9 (Eu $4f^7$) and 10 (Sm $4f^6$) only the exchange-split high-binding-energy states are broadened by the decay effect, and the low-energy spectral features are alike for the spectra convoluted with constant Γ and with term-dependent Γ_f plus Gaussian. It should be added that the small structure near 125 eV in the experimental spectrum of Sm metal [Fig. 10(a)] is due to divalent component at the surface, so that it was ignored.

IV. DISCUSSION

In the preceding section it was shown that the multiplet term dependence of the lifetime broadening was essential to reproduce the $4d$ -XPS in heavy rare-earth elements. In this section we will discuss the mechanism of this dependence in the first place and then discuss other problems.

We begin with the $Gd^3 (4f^7)$ ion, as a simple example. We saw that the spectrum was split into two parts by exchange interaction, and that the broadening widths of the lower- (higher-) binding-energy states are small (large).

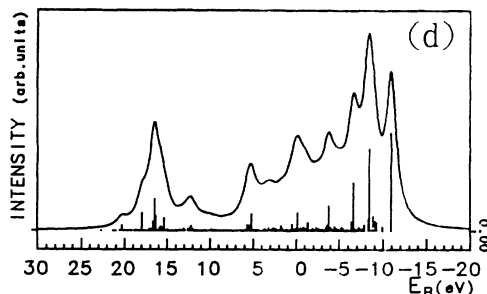
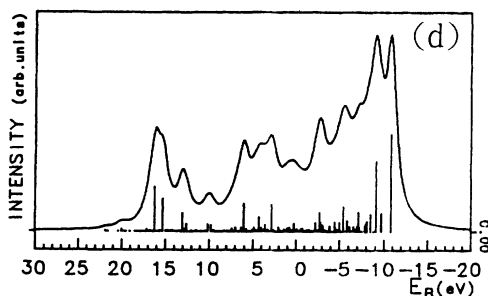
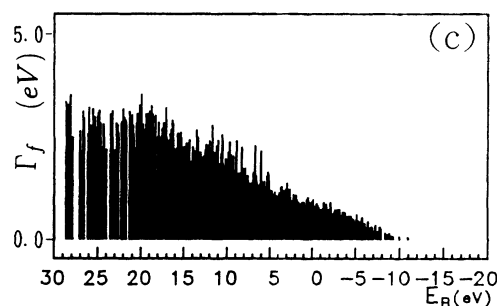
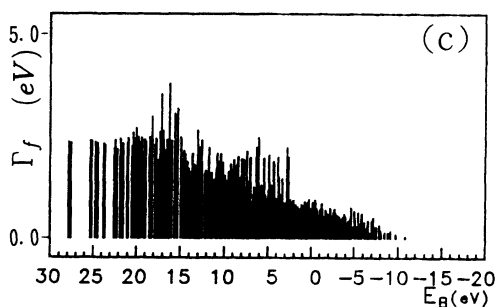
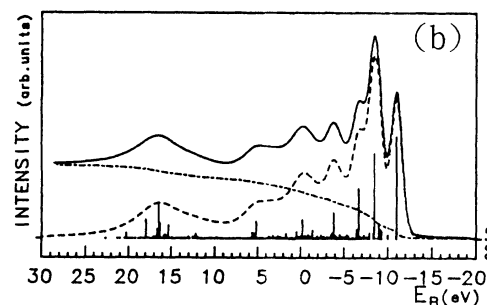
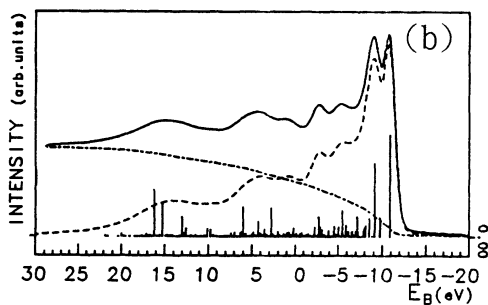
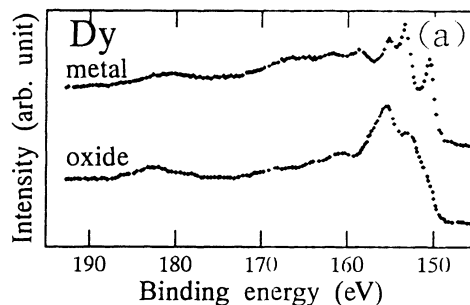
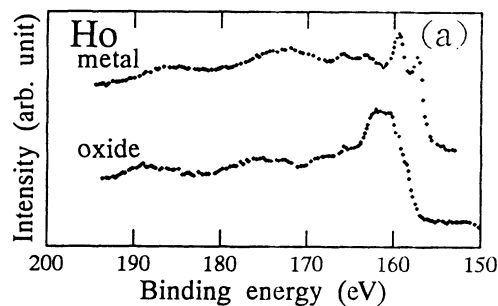


FIG. 5. Experiments and calculation for Ho.

FIG. 6. Experiments and calculation for Dy.

This can be explained by a spin-selection rule as shown in Fig. 11(a).

The spin of the 4*f* shell is stretched to its maximum value according to Hund's rule. The binding energy of the final states strongly depends on the spin direction of the core hole in the 4*d* orbit. If the spins of the 4*f* shell and 4*d* core are parallel (antiparallel), the states appear in the low- (high)- binding-energy region because of the large exchange interaction. The 4*d*-4*f*4*f* s-CK decay process also strongly depends on the direction of spins. In this process the decay of spin-parallel states is not al-

lowed by the spin-selection rule as can easily be seen in Fig. 11(a), while that of the antiparallel states is allowed. This explains why the lower binding energy states are long lived and sharp, and why the higher ones are short lived and broad.

The same argument can be applied to lighter rare-earth elements, such as Eu and Sm. These materials have very sharp peaks near the edge and broad structure in high-binding-energy region. In light rare earths, however, the

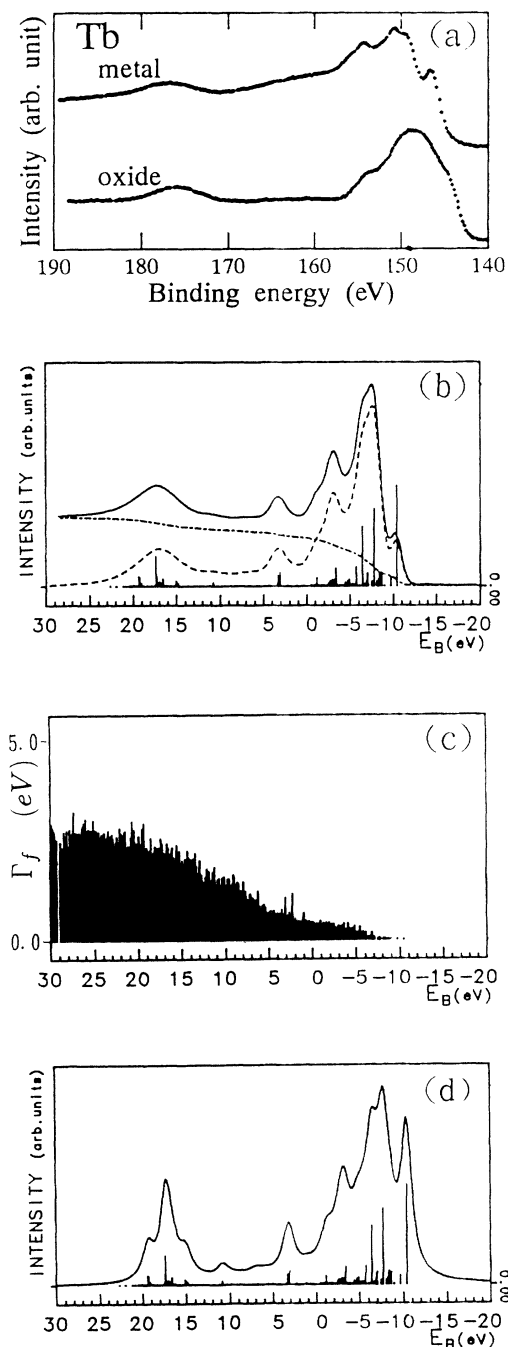


FIG. 7. Experiments and calculation for Tb.

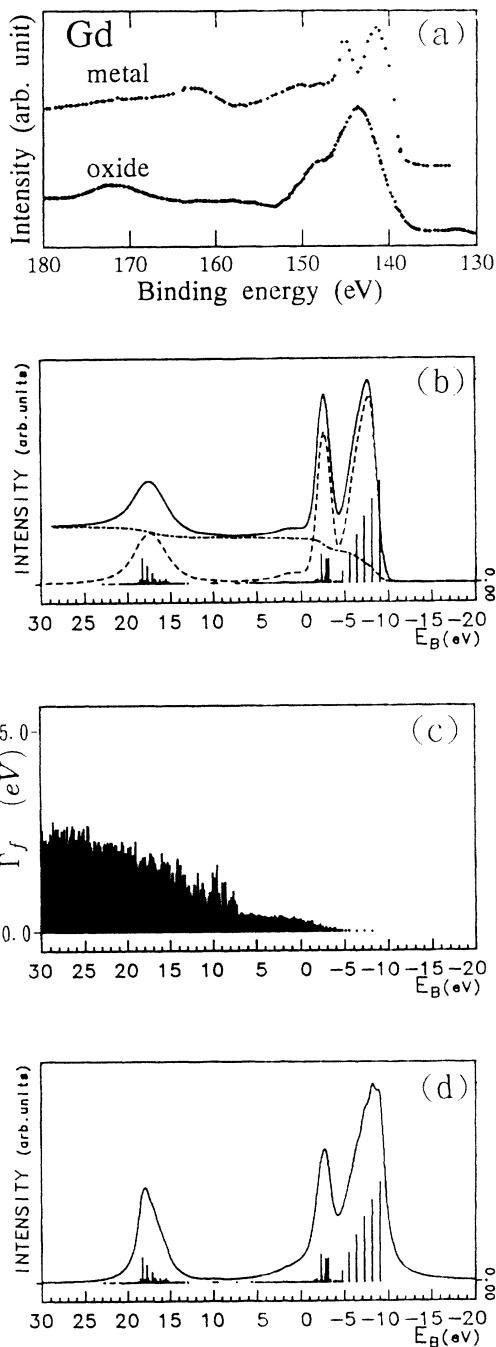


FIG. 8. Experiments and calculation for Gd. Experiments are taken from Ref. 3 (metal) and Ref. 6 (oxide). The origin of binding energy for oxide is taken arbitrary.

role of the decay channels other than $4d-4f4f$ s-CK becomes relatively important and may not be ignored, because the number of $4f$ electron is small.

If the $4f$ shell is more than half filled, the decay process of the lower-binding-energy states becomes possible and the width of these states becomes broader. However, it is difficult to explain all the tendencies by the spin-selection rule, for example, why the Yb^{3+} ion, which has an almost filled $4f^{13}$ shell, still shows lifetime dependence or why the lifetime broadening Γ_f seems to vary linearly to binding energy.

These facts could be understood from the viewpoint of

electron correlation. The multiplet splitting of $4d$ -XPS is dominated by the $4d-4f$ exchange interaction. The lower-energy states are those which spin-parallel electrons (or holes) are separated by Pauli exclusion principle, while the higher are those states which spin-antiparallel electrons are strongly interacting. The electron correlation affects the spin-anti-parallel states in multiplets, which states are excessively interacted in the first-order splitting. If we consider the configuration interaction such as $4d-4f4f$ s-CK, we take into account the correlation between spin-antiparallel electrons. This effect is expressed as self-energy in the previous section,

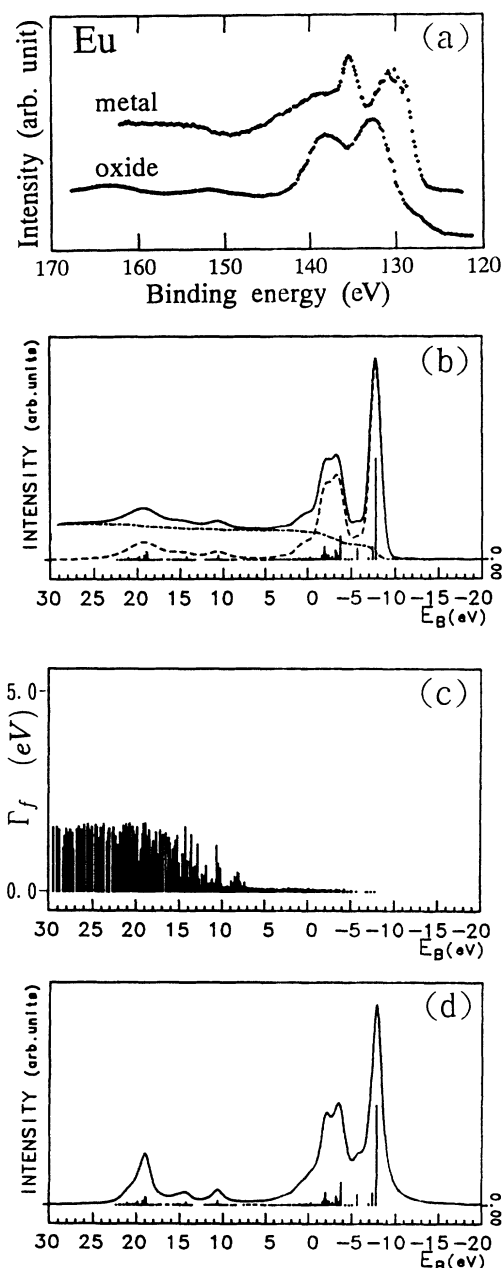


FIG. 9. Experiments and calculation for Eu. Experiments are taken from Ref. 3 (metal) and Ref. 6 (oxide). Eu metal is divalent. The origin of binding energy for oxide is taken arbitrary.

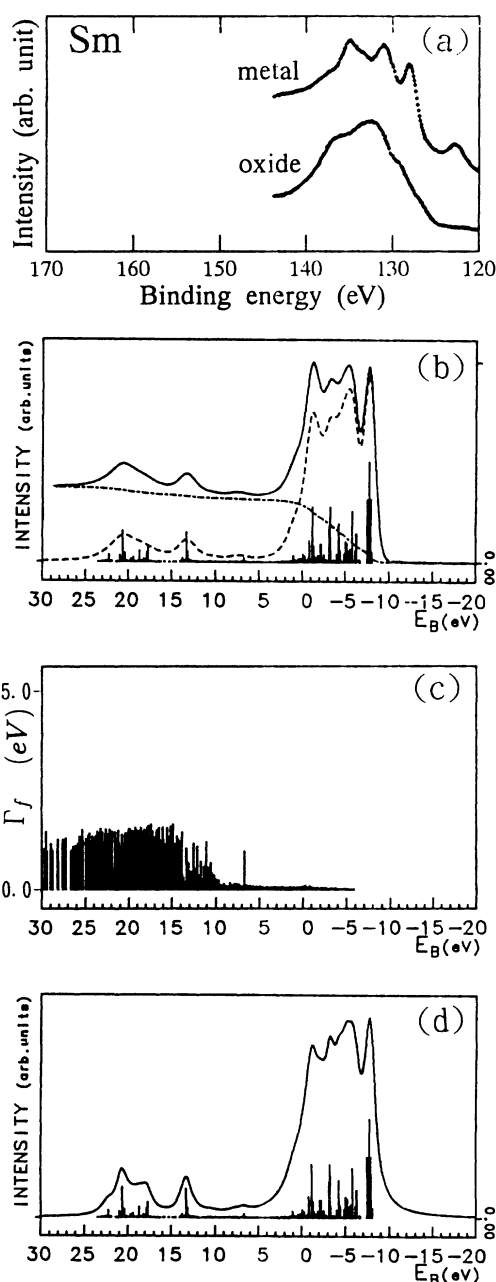


FIG. 10. Experiments and calculation for Sm. Experiments are taken from Ref. 5, the exchange-split high-binding-energy part is not present in this experiment.

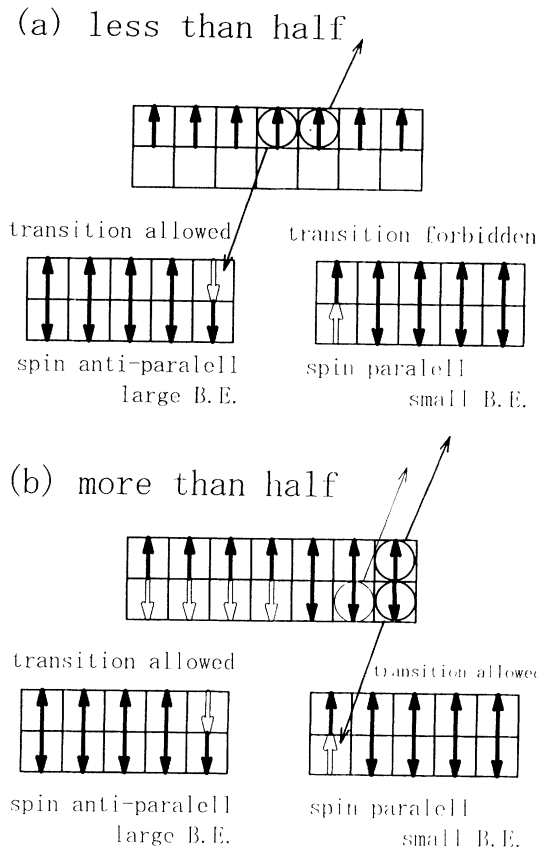


FIG. 11. Schematic diagram of spin selection rule for s-CK decay.

by which the energy shift and the lifetime broadening are expressed.

Because the largest higher-order interaction in this case is the CI between continuum states by s-CK decay, the higher-binding-energy states are more broadened than the lower-energy ones. If the energy splitting of the multiplet is dominated by the exchange interaction, the higher-binding-energy states suffer the larger self-energy correction. The linearity (although not exact) between the broadening and the binding energy can be confirmed by the calculation without spin-orbit and direct Coulomb interaction.

In the case of 3d-XPS in rare-earth elements, although spin-orbit interaction of 3d hole is the largest, the coupling between core hole and 4f shell is still strong. The spectra, however, do not seem to show strong multiplet dependence of lifetime. This may be due mainly to the processes such as 3d-4(s,p,d)4(s,p,d) Auger decay, which do not depend on multiplet because of the filled 4(s,p,d) shells.

From the experiments in the figures, it is noticed that the spectral shape of the metal and oxide are different for the elements besides Yb and Eu. The valence mixing effect can be excluded for those elements from the analysis of 3d-XPS. We think these differences would not be intrinsic. The experiment for oxide can be reproduced if we use larger Gaussian broadening width. In Fig. 12, we show the calculation with different Gaussian width for

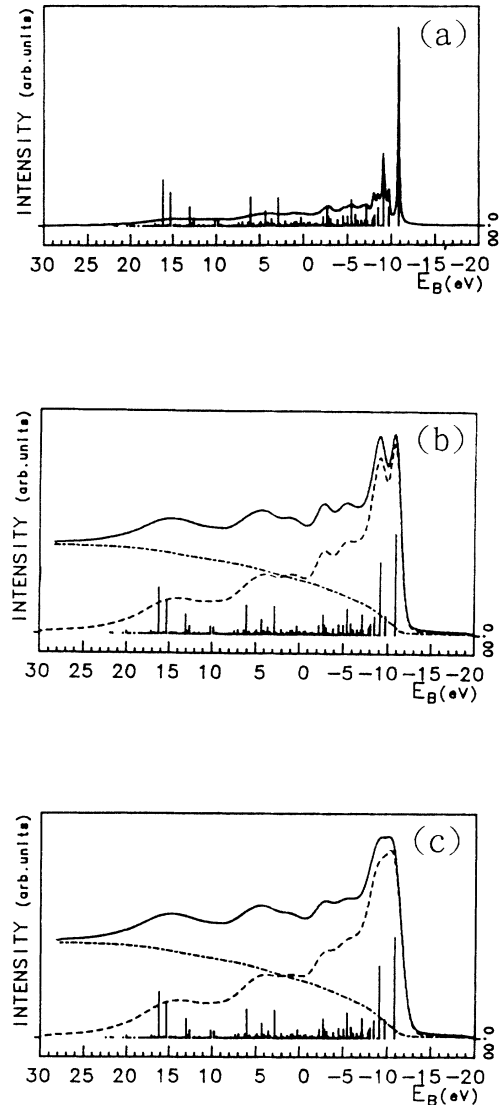


FIG. 12. Calculation with different instrumental resolution for Ho^{3+} ion, (a) ideal resolution, (b) calculation with Gaussian of 0.7 eV (HWHM), (c) calculation with Gaussian of 1.0 eV (HWHM).

Ho as an example. Figure 12(a) is the spectrum without Gaussian broadening, in Figs. 12(b) and 12(c) their widths are taken to be 0.7 eV (HWHM) and 1.0 eV (HWHM), respectively. Figures 12(b) and 12(c) reproduce the spectra for metal and oxide fairly well. This also holds for other elements. It is possible that the charge-up effect or some inhomogeneous chemical shifts make the resolution worse for the oxides.

V. SUMMARY

In this paper we discussed the lifetime effect on the multiplet structure of the 4d-XPS in heavy rare-earth elements. It was shown that the lifetime broadening has term dependence and that the s-CK decay process in the final state of XPS has a strong effect on the whole shape of the spectrum. The generally adopted procedure of convoluting the calculated line spectra by a constant

broadening Γ cannot reproduce the experiment at all. The same situation is expected when the coupling between a core hole and an unfilled valence shell is strong and at the same time the decay process is dominated by the interaction between these shells. We have already discussed this effect on the $3p$ -XPS in transition-metal compounds ($3p$ - $3d$ coupling),¹⁵ and the same effect might be found in $5d$ -XPS in actinide compounds ($5d$ - $5f$ coupling).

Some complementary information would be acquired from the Auger electron spectroscopy (AES), in which the Auger electron emitted by the $4d$ - $4f$ $4f$ s-CK process is detected, and from the x-ray emission spectroscopy (XES), in which the x-ray is emitted by the $4f \rightarrow 4d$ transition.¹⁶ The contribution of the decay process other than $4d$ - $4f$ $4f$ s-CK decay could be estimated from these experiments.

We have neglected the real part of the self-energy and approximated the effect by the reduction of the Slater integrals. It might be interesting to treat the many-body effect more strictly and calculate the self-energy explicitly. Because the real part and the imaginary part of the self-energy are connected by the Hilbert transformation, the reduction of splitting width and the lifetime broadening of a multiplet are correlated. Both effects are two different aspects of the electron correlation. We can also estimate from this calculation how much of the reduction is due to the $4d$ - $4f$ $4f$ decay effect and how much to the other.

Wendin and Ohno¹⁷ have made a more realistic estimation of the self-energy for the $4p$ -XPS in a Xe atom, although they have neglected the multiplet effect except for spin-orbit coupling. Their results reproduce both the absolute binding energy and the spectral broadening fairly well. The lifetime broadening of the $4p_{1/2}$ and $4p_{3/2}$ spin-orbit components are quite different. Here the lifetime, however, depends on whether the peak is above or below the $4p$ - $4d$ $4d$ (ϵf) super-Coster-Kronig decay threshold. The essential difference between their case

and ours is that in our case all of the multiplets are above the threshold and the symmetry of multiplet terms causes the difference in the decay probabilities.

The concept of the one-electron orbit or lifetime of a core hole is not valid for the case where the coupling between the core hole and unfilled valence shell is strong. It can be said that the central field approximation in the HF calculation is not good for this case, so that one cannot ignore the rest of electron-electron interaction, that is noncentral interaction. The strong deviation from the spherically averaged Hartree-Fock potential is the main cause of both the large multiplet splitting and the strong s-CK decay.

The multiplet structure is the first-order perturbation calculation, and the configuration interaction is the higher order. Auger transition is a CI perturbation with continuum states. Because the highly correlated states have larger CI perturbation, they are mixed with continuum states and become quasibound states. It is quite natural that the highly correlated states (i.e., high-binding-energy terms) suffer the larger correction and that they have shorter lifetime. It can be said in one way that the lifetime dependence is due to the selection rule of Auger transition or in another way that it is due to the correlation effect between the core hole and unfilled valence shell. The multiplet structure and the variation of the lifetimes are one thing seen from two points.

ACKNOWLEDGMENTS

This work was supported in part by the Grant-in-Aid for Scientific Research (International Scientific Research Program) from the Ministry of Education, Science and Culture of Japan. One of the authors (H.O.) received financial support during this work from Fellowship of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

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