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Origin of the high-binding-energy structure in the 3d core-level spectra of divalent Eu compounds

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The high-binding-energy structure in the Eu 3d core-level x-ray photoelectron spectra of divalent Eu compounds, which has been ascribed as the "shakeup" satellite, is shown to be due to the multiplet structure of $3d4f^7$ (bar denotes a hole) final-state configuration. Hence, the apparent inconsistency between this so-called high-energy probe and low-energy probes for the valence of these Eu compounds is resolved.

Rare-earth metals and their compounds have been the subject of extensive study because of the valence fluctuation phenomena¹ and heavy fermion properties,² which originate from the interaction between highly correlated 4f electrons and delocalized conduction electrons. Core-level x-ray photoelectron spectroscopy (XPS) has been very valuable in studying electronic structures of these compounds. Core-level spectra can be usually understood by the following Anderson impurity Hamiltonian including the Coulomb interaction between the core hole and 4f electrons:^{3,4}

$$\begin{aligned}
 H = \sum_{\nu=1}^{N_f} \left[\int \epsilon \varphi_{\epsilon\nu}^+ \varphi_{\epsilon\nu} d\epsilon + [\epsilon_f - U_{fc}(1-n_c)] \varphi_{\nu}^+ \varphi_{\nu} \right. \\
 \left. + \int [V(\epsilon) \varphi_{\nu}^+ \varphi_{\epsilon\nu} + V(\epsilon)^* \varphi_{\epsilon\nu}^+ \varphi_{\nu}] d\epsilon \right] \\
 + U_{ff} \sum_{\mu>\nu} n_{\mu} n_{\nu} + \epsilon_c n_c, \quad (1)
 \end{aligned}$$

where ϵ describes the energy of the conduction-band state, ϵ_f is the energy of the 4f level, and ϵ_c describes the energy of a core level. The 4f level has N_f -fold degeneracy, whose quantum numbers are denoted by μ, ν . The hopping between the 4f level and the conduction state is described by $V(\epsilon)$ and the Coulomb interaction between 4f electrons is given by U_{ff} , where in the simple model multiplet effects are neglected. U_{fc} is the Coulomb interaction between a core hole and an f electron. Thus while the $|f^n\rangle$ and $|f^{n+1}\rangle$ states are nearly degenerate in energy in the initial state, they have an energy separation of U_{fc} in the final state of photoemission, because the en-

ergy of the $|f^n\rangle$ state is pulled down by the amount nU_{fc} (n is the number of f electrons) by the core hole created in photoionization. This gives rise to the satellite structure in the deep core-level XPS spectra, whose intensity depends on the strength of $V(\epsilon)$ and the energy position of ϵ_f . Therefore, by analyzing deep core-level XPS spectra, we can get information of the valence electronic structure. For this purpose 3d core-level spectra usually used because 4d core-level XPS shows very complicated multiplet structures due to the strong interaction between the 4d hole and unfilled 4f shell (they have the same principle quantum number $n=4$).

Many Ce compounds and several Yb compounds have been studied by the core-level XPS technique, and they are shown to be consistent with physical properties measured by so-called low-energy probe techniques such as Mössbauer isomer shift and the magnetic susceptibility.^{4,5} However, for some Eu compounds the results of high-energy probes such as photoemission spectroscopy (PES) and x-ray absorption spectroscopy do not seem to be consistent with those of low-energy probes. For example, the Eu 3d core-level XPS spectra of EuAg₅, EuPd₂P₂, and EuCu₅, which are known to be divalent in the ground state by Mössbauer isomer shift and magnetic susceptibility measurements,⁶⁻⁸ are reported to show two peaks, one corresponding to the divalent ($4f^7$) configuration and the other at about 6.5–8.0 eV higher-binding-energy side of the divalent peak.⁸⁻¹⁰ This double-peak structure is characteristic of the mixed-valent compounds, and the extra peak at the high binding energy is presumed to be due to the trivalent ($4f^6$) configuration as judged by the energy position.

This extra "trivalent" peak has been ascribed as the

"shakeup satellite" arising from the final-state effect in the photoemission process.⁸⁻¹⁰ The final-state effect is due to the Coulomb interaction of the created photohole with the electronic system, and it may lead to a change of the $4f$ electron occupation number in the final state and an apparent change of the valence. The well-known example is the shakedown process, where a satellite appears at the lower-binding-energy side of the main peak. This happens because an unoccupied initial $4f$ state is lowered in energy by the potential of the photohole and becomes occupied by a conduction electron in the final-state screening process. This process is well understood within the Gunnarsson-Schönhammer model calculation of the Anderson impurity Hamiltonian^{3,4} shown in Eq. (1) above, and the intensity of the observed shakedown satellite has been used to determine *quantitatively* the hybridization strength between the $4f$ and conduction-band states in many light rare-earth systems.⁵

At first sight, one might suppose a similar approach can be applied in the interpretation of the Eu $3d$ spectra of divalent Eu compounds in question. However, there are serious fundamental problems with this interpretation. First of all, in metallic systems usually a *shakedown* satellite appears in the lower-binding-energy side of the main peak because of screening. A *shakeup* process, as proposed in Refs. 8-10 where a satellite appears in the higher-binding-energy side of the main peak, is highly unlikely and has never been positively identified in metals. In a shakeup excitation a localized $4f$ electron should be scattered into the conduction band similarly to an autoionization effect. Such a process is known to occur in atomic and molecular spectroscopy, but no quantitative model which can be applied to the solid-state system has yet been proposed. Second, even if we were to apply the Gunnarsson and Schönhammer formalism blindly, we find that the observed intensity of the satellite (about 15% of the main peak) cannot be made compatible with the purely divalent ground state because the hybridization strength turns out to be very large owing to the large energy separation between the ($3d4f^7$) and ($3d4f^6$) configurations. We can explore the possibility of using different hybridization strengths for the initial and final states,¹¹ but even then the hybridization strength required for the final state is too large to be deemed reasonable (much larger than typical α -like Ce compounds⁵ contrary to the expectation of the lanthanide contraction).

Hence, we have studied several divalent Eu compounds (EuPd, EuAg₅, EuAu₅) in detail in order to understand the origin of these so-called shakeup satellites in the Eu $3d$ core-level XPS spectra of divalent Eu compounds. In this paper, we will report only the results on EuAu₅ because in EuPd and EuAg₅ some Auger emissions overlap with Eu $3d_{5/2}$ or $3d_{3/2}$ core-level spectra so that quantitative analyses on both spin-orbit components are difficult. However, the results for EuPd and EuAu₅ are consistent with the interpretation given below, and their spectra along with those of several trivalent Eu compounds will be reported in detail in a separate publication.¹²

The EuAu₅ sample was the polycrystalline ingot which was grown in the vacuum furnace with a SiC heater,

where appropriate amounts of elements were sealed in the quartz tube with an alumina boat. This sample was annealed after growth and the crystal structure and the stoichiometry were checked by x-ray analysis. Just before taking PES spectra, the sample was scraped repeatedly by a diamond file *in situ* in the preparation chamber at the pressure better than 2×10^{-10} torr to get fresh surfaces, and transferred to the analysis chamber without breaking the ultrahigh vacuum. The $3d$ core photoemission spectrum was measured using a photoemission spectrometer manufactured by VSW Scientific Instruments Ltd. in England, which was equipped with concentric hemispherical analyzer with a multichannel detector system. As a photon source, Al $K\alpha$ source was used. The operating power of the x-ray source was 150 W (10 kV, 15 mA). During the experiments the analysis chamber pressure was maintained better than 3.5×10^{-10} torr. Sample cleanliness was checked by monitoring oxygen and carbon 1s peaks.

Figures 1(a) and 1(c) show the Eu $3d_{5/2}$ and $3d_{3/2}$ core-level XPS spectra of the EuAu₅ compound, respectively. As mentioned before, EuAu₅ is known to be divalent in the ground state according to the results of magnetic susceptibility and Mössbauer isomer shift measurements.¹³ However, we find in these XPS spectra that there are two peaks, the main peak and a satellite in the high-binding-energy region in both Eu $3d_{5/2}$ and $3d_{3/2}$

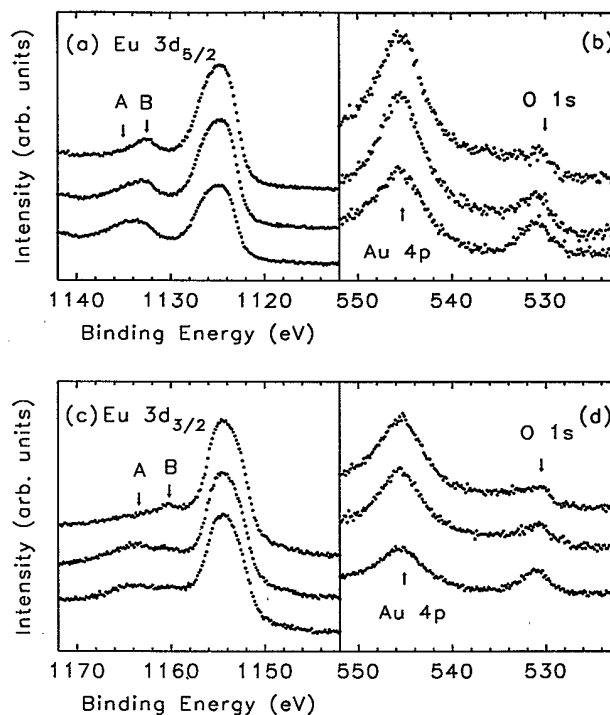


FIG. 1. The Eu (a) $3d_{5/2}$ and (c) $3d_{3/2}$ core-level spectra of the EuAu₅ compound and the O 1s [(b), (d)] spectra obtained with the Al $K\alpha$ x-ray source. Arrows A and B in (a) and (c) represent peaks due to the oxidized phase Eu₂O₃ and due to the intrinsic structure, respectively. (b) and (d) show the variation of the O 1s spectra as the contamination from the Eu₂O₃ phase increases from the top. In the higher binding side of the O 1s peak lies the Au 4p peak.

spin-orbit component spectra. This is similar to previous reports,⁸⁻¹⁰ and the satellite peak intensity relative to the main peak is also similar to (although slightly smaller than) the published spectra of EuCu_5 and EuPd_2P_2 .¹⁴

Before discussing the origin of this satellite, we have to make sure that it is not due to an extrinsic effect such as oxygen contamination, because the stable form of Eu oxide is Eu_2O_3 which can give rise to the trivalent Eu peak. In order to check for this possibility, we took the oxygen 1s spectra simultaneously with the Eu 3d spectra and show them side by side in Figs. 1(b) and 1(d). The amount of the oxygen level can be estimated by the relative weight of the O 1s peak to the Au 4p peak shown in the same figure. We can see in this figure that the structure in the high-binding-energy region of the Eu 3d core XPS spectra actually grows with the increase of the oxygen quantity. However, if we look more closely, especially in the top spectra where the oxygen level is lowest, we find that the structure in the high-binding-energy region actually consists of two peaks *A* and *B*, one of which (peak *A*) grows with the oxygen level but the other peak *B* does not change its intensity with oxygen. Hence, we conclude that peak *B* is an intrinsic peak not related to the oxygen contamination, where peak *A* probably comes from the oxidized Eu_2O_3 phase. That is, although some of the intensity of the so-called shakeup satellite reported in the literature may have come from the slight oxidation of the sample surface, there is still some intrinsic parts that remain to be explained.

To determine the energy position and the intensity of the intrinsic peak *B* relative to the main peak, we analyzed the Eu 3d spectra by the curve fitting method as described in our previous paper on Yb compounds.¹⁵ The energy separation between the main peak and peak *B* thus found is about 8.05 eV for the Eu $3d_{5/2}$ spectrum and 6.5 eV for the Eu $3d_{3/2}$ spectrum. The intensity of peak *B* was found to be about 9% of the main peak in the Eu $3d_{5/2}$ spectrum and about 11% in the Eu $3d_{3/2}$ spectrum. Similar results were obtained from the analyses of the Eu 3d spectra of other divalent Eu compounds EuPd and EuAg_5 we have studied.¹²

Now, what is then the origin of this intrinsic satellite in the Eu 3d XPS spectra? The fact that the energy separation and intensity ratio between the main and satellite peaks is different depending on the spin-orbit component ($3d_{5/2}$ and $3d_{3/2}$) rules out many conventional mechanisms such as plasmon excitation or simple shakeup satellite models. It turns out that the answer is quite simple, *a part of the multiplet structure of the $3d4f^7$ final-state configuration*. In Fig. 2, we show with solid lines the calculated spectra of the $3d^{10}4f^7 \rightarrow 3d^94f^7 + \text{photoelectron}$ transition in the intermediate coupling scheme, and compare them with our experiment data. We can see that the theory predicts the position and intensity of the intrinsic peak *B* very nicely for both $3d_{5/2}$ and $3d_{3/2}$ components. In particular, the calculation predicts that the binding energy and the intensity of the satellite peak in the high-binding-energy region relative to the main peak for the $3d_{3/2}$ core spectrum are different from those for the $3d_{5/2}$ core spectrum, as observed in the experiments. Even the asymmetric line shapes of main peaks are as predicted.

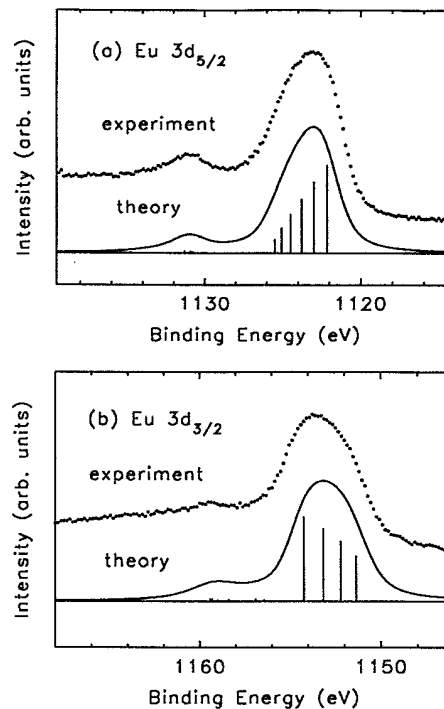


FIG. 2. The comparison between the experimental spectra (dots) and the calculated multiplet structures from intermediate-coupling scheme (solid lines) of the (a) Eu $3d_{5/2}$ and (b) Eu $3d_{3/2}$ spin-orbit components for the divalent Eu^{2+} compounds. The theoretical line spectra are convoluted with the Lorentzian (full width=1.4 eV) and Gaussian (full width=1.4 eV) functions to simulate the experimental spectra. The main peaks of the theoretical curves were aligned in energy in the experimental main peak positions.

The satellite is a superposition of many (more than 50) final-state multiplet lines, and the calculated sum of their intensities relative to the main peak is about 10% for the $3d_{5/2}$ component and $\sim 12\%$ for the $3d_{3/2}$ component. These numbers compare well with the experimental values of $\sim 9\%$ and $\sim 11\%$, respectively.

In this calculation, the $4f^7$ ground-state and the $3d^94f^7$ final-state multiplets were calculated using basis sets spanned by all the possible states of the configuration. The electrostatic interactions between 4f electrons, those between 3d and 4f electrons, and the spin-orbit interactions in the 3d and 4f levels were all taken into account using the parameter values given by Thole *et al.*¹⁶ The resulting line spectrum was convoluted with the Lorentzian function of full width 1.4 eV and the Gaussian function of full width 1.4 eV to simulate the lifetime and the instrumental broadening, respectively.

It may seem somewhat surprising that the multiplet structure of the $3d4f^7$ final state gives rise to an apparent "satellite peak" separated from the "main" structure by 6.5–8.0 eV in energy for this Eu^{2+} configuration. Usually in many rare-earth components studied so far, including Ce, Pr, Nd, and Yb compounds,^{4,17-19} the multiplet structure of the $3d4f^n$ configuration in the 3d core-level spectra gives rise to only the broadening of the peak within the lifetime and experimental resolution, but never a separate peak structure as in this case. The reason for

the occurrence of this double-peak structure for the divalent Eu compounds is the large Hund's rule stabilization energy of the $4f^7$ state and the exchange interaction between $3d$ and $4f$ electrons in the final state. The main peak in the $3d$ core-level spectra consists of multiplets of the type $|4f^7: {}^8S\rangle|3d^9j\rangle$, where j is the total angular momentum of the core hole (either $\frac{3}{2}$ and $\frac{5}{2}$). In these configurations spins of all seven $4f$ electrons are aligned to give the total spin momentum of $S = \frac{7}{2}$ to gain the maximum Hund's rule exchange energy as in the ground state. On the other hand, deviation of the $4f^7$ configuration from 8S into sextets ($S = \frac{5}{2}$) leads to the satellite. This process always includes spin flip of one $4f$ electron, and because the Hund's rule energy is large the resulting multiplets are quite separate in energy from the main peak. A relevant process creating these configurations is the exchange of a $4f$ electron with a $3d$ electron in the final state due to the electrostatic interaction between them, since the spin-orbit interaction of the $4f$ electron is rather small. Here, a $4f$ electron fills the $3d$ hole and a $3d$ electron with the opposite spin is transferred to the $4f$ level. The nondiagonal matrix element of the electrostatic interaction corresponding to this process is about 1 eV, which is large enough to create the "satellite" of appreciable intensity.

One might think that small amounts of the 6P and 6D states mixed in the ground state for the Eu^{+2} configuration can be the origin of the satellite, since the calculation in the intermediate coupling scheme gives the ground state of the divalent Eu metal as follows:²⁰

$$|\psi_g\rangle = 0.9869|f^7: {}^8S_{7/2}\rangle + 0.1600|f^7: {}^6P_{7/2}\rangle - 0.0117|f^7: {}^6D_{7/2}\rangle.$$

We checked for this possibility by calculating the XPS multiplet spectrum from the pure 8S initial state. The results showed no significant difference compared with the spectrum from the real ground state, and it can be concluded that the initial-state mixing is not responsible for

the satellite structure.

The above interpretation for the origin of the satellite is also confirmed by the core-level XPS of GdF_3 , a trivalent Gd compound with the same $4f^7$ configuration as Eu^{2+} . The Gd $3d$ XPS of GdF_3 published in Ref. 21 indeed show similar satellites in both $3d_{3/2}$ and $3d_{5/2}$ components, although with reduced intensity as expected from the higher stability of the Gd $4f^7$ configuration. This result rules out the surface oxidation or the initial-state mixing as the possible origin of the satellites, and confirms the multiplet structure picture.

We should mention here that a so-called shakeup satellite structure has also been proposed in the Eu L_{III} absorption spectrum of EuPd_2P_2 .²² The multiplet mechanism as applied to the Eu $3d$ XPS does not seem to be applicable in this case because the exchange interaction between the $2p$ hole and $4f$ electrons is not strong enough to produce a satellite of appreciable intensity. Further investigations, both experimental and theoretical, seem necessary to elucidate the existence and the origin of this structure.

In summary, by analyzing the Eu $3d_{5/2}, 3d_{3/2}$ core-level XPS spectra of the divalent EuAu_5 compound carefully, we conclude that the so-called shakeup satellite peak structure in the high-binding-energy region of the Eu $3d$ core-level XPS spectra for divalent Eu compounds is nothing but the multiplet structure of the $3d4f^7$ final-state configuration. Hence, the apparent inconsistency between this high-energy probe and the results of low-energy probes is resolved.

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

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

³O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

⁴J.-S. Chung, E.-J. Cho, and S.-J. Oh, Phys. Rev. B **41**, 5524 (1990).

⁵J. W. Allen, S.-J. Oh, O. Gunnarsson, K. Schönhammer, M. B. Maple, M. S. Torikachvili, and I. Lindau, Adv. Phys. **35**, 275 (1986).

⁶E. V. Sampathkumaran, B. Perscheid, and G. Kaindl, Solid State Commun. **51**, 701 (1984).

⁷F. J. Van Steenwijk, H. Th. Lefever, R. C. Thiel, and K. H. J. Buschow, Physica B & C **79B**, 604 (1975).

⁸C. Laubschat, B. Perscheid, and W.-D. Schneider, Phys. Rev. B **28**, 4342 (1983).

⁹W.-D. Schneider, C. Laubschat, I. Nowik, and G. Kaindl, Phys. Rev. B **24**, 5422 (1981).

¹⁰G. K. Wertheim, E. V. Sampathkumaran, C. Laubschat, and G. Kaindl, Phys. Rev. B **31**, 6836 (1985).

¹¹O. Gunnarsson and O. Jepsen, Phys. Rev. B **38**, 3568 (1988).

¹²E.-J. Cho, S.-J. Oh, S. Suga, T. Suzuki, and T. Kasuya (unpub-

lished).

¹³F. J. Van Steenwijk, W. J. Huiskamp, H. Th. Lefever, R. C. Thiel, and K. H. J. Buschow, Physica B & C **86-88B**, 89 (1977).

¹⁴The published spectra of EuAg_5 (Ref. 8) show much stronger satellite intensity than Fig. 1, but we confirmed that this is due to the oxidation. See Ref. 12 for details.

¹⁵E.-J. Cho, J.-S. Chung, S.-J. Oh, S. Suga, M. Taniguchi, A. Kakizaki, A. Fujimori, H. Kato, T. Miyahara, T. Suzuki, and T. Kasuya, Phys. Rev. B **47**, 3933 (1993).

¹⁶B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteve, Phys. Rev. B **32**, 5107 (1985).

¹⁷S. Imada and T. Jo, Phys. Scr. **41**, 115 (1990); J. Phys. Soc. Jpn. **58**, 402 (1988).

¹⁸N. Spector, C. Bonnelle, G. Dufour, C. K. Jorgensen, and H. Berthou, Chem. Phys. Lett. **41**, 199 (1976).

¹⁹Y. Kim, S.-J. Oh, and Z. G. Khim, J. Korean Phys. Soc. **23**, 153 (1990).

²⁰F. Gerken, J. Phys. F **13**, 703 (1983).

²¹K. H. Park and S.-J. Oh, Phys. Rev. B **48**, 14 833 (1993).

²²E. V. Sampathkumaran, G. Kaindl, W. Krone, B. Perscheid, and R. Vijayaraghavan, Phys. Rev. Lett. **54**, 1067 (1985).