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Shake-up excitations and core-hole screening in Eu systems

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X-ray photoemission (XPS) spectra of the Eu $3d$ and Eu $4d$ core levels in Eu metal and in divalent and trivalent Eu compounds exhibit splittings into two components, caused by the occurrence of $4f^6$ and $4f^7$ final-state configurations. The observed phenomena are described in terms of final-state shake-up and shake-down processes accompanied by a decrease, respectively, increase of the $4f$ occupation number. An extension of the Kotani-Toyozawa model to f and d states gives a consistent description of both processes.

Quite frequently, core-level photoemission (PE) spectra of light rare-earth (RE) solids exhibit—in addition to well-known multiplet splittings—a characteristic satellite structure, which has been attributed to final-state effects.[1–4] Mainly on relative intensity arguments high-binding-energy (shake-up) and low-binding-energy (shake-down) satellites were identified. Recently, the underlying mechanism for these processes became better understood: The effective increase of the core potential during photoionization causes a deformation of the local density of states, which in turn can lead to a change of the $4f$ occupation number in the final state.[5,6]

The case usually encountered is characterized by an *increase in the 4f occupation number* in the final state. Depending on the final-state position of the unoccupied $4f$ state relative to the valence-band-edge energy-gain (shake-down) or energy-loss (shake-up) satellites have been discussed.[2] Assuming an increase in the $4f$ occupation number to be energetically favored Fuggle *et al.*[4] attributed, e.g., the observed $3d$ structures of Ce compounds to well-screened (low-binding-energy) and poorly screened (high-binding-energy) states. A second process for shake up was proposed by Wertheim and Campagna[7] according to which the number of $4f$ electrons remains constant, but an excitation to higher multiplet levels within the $4f$ shell takes place. Such a shake-up process has not been identified so far. A third possibility for a shake-up process is given by a *decrease in the 4f occupation number* connected with the transition of a localized $4f$ electron to an unoccupied valence state. This process has not yet been considered in interpreting RE XPS (x-ray photoemission) spectra. In this Communication we show the occurrence of such a shake-up excitation and a corresponding shake-down process in integral-valent Eu compounds. On the basis of split $3d_{5/2}$ and $4d$ core levels the presence of both $4f^6$ and $4f^7$ final-state configurations are identified in Eu^{2+} and Eu^{3+} compounds. Support for this identification is given by theory: Calculations by Johansson[8] and by Herbst and Wilkins[9] agree well with the observed splittings. It is shown that an extension of the Kotani-Toyozawa (KT) model[5] to f and d states gives a consistent description of shake-up and shake-down processes in core-level photoemission. Finally, implications of this model for the interpretation of XPS spectra of Ce compounds are discussed.

The XPS measurements were performed with a VG-ESCA-3 spectrometer with a total resolution of $\simeq 1$ eV, which is mainly due to the linewidth of the Al $K\alpha$ x rays. The sample surfaces were mechanically cleaned in a vacuum of 4×10^{-10} Torr, and this process was frequently repeated to keep the oxygen contamination below the limit of detectability (by monitoring the O $1s$ signal). The samples of $EuAl_2$, $EuPd_3$, and $EuRh_6B_4$ were prepared by arc melting in Ar atmosphere and were characterized as described in Refs. 10 and 11. Eu_2O_3 surfaces were prepared by oxidation of the $EuPd_3$ sample and independently by using a pressed-powder sample of Eu_2O_3. In order to determine the initial-state valence of the studied Eu solids, ^{151}Eu Mössbauer spectra and magnetization data were taken. These measurements clearly show that the studied materials have integral valences in the ground state (Eu^{2+}:Eu, $EuAl_2$; Eu^{3+}:$EuPd_3$, $EuRh_6B_4$, Eu_2O_3).

XPS spectra of the Eu $3d_{5/2}$ core-level region are shown in Fig. 1 for the five studied Eu solids. It is striking that both for Eu^{2+} and Eu^{3+} systems the $3d_{5/2}$ line is split into two compounds (by 7.8 ±0.2 eV in Eu metal and by 9.0 ±0.2 eV in Eu_2O_3), with varying relative intensities. The shapes and widths of the two components are somewhat different, which can be expected due to multiplet splitting for two different final-state $4f$ configurations. Recently, Crecelius *et al.*[2] and Herbst *et al.*[3] have shown that due to the stability of the half-filled $4f$ shell in Eu^{2+} the $4f^7$ and $4f^8$ final states coincide energetically within the linewidth of the Eu $3d_{5/2}$ core level. Therefore, the observed splittings of the core-level XPS lines in Eu^{2+} and Eu^{3+} compounds must be interpreted as a consequence of Eu $4f^6$ and Eu $4f^7$ final-state configurations. A further confirmation for the correctness of this identification is given by the magnitude of the observed splittings. Using an equivalent-core argument, in which trivalent core-ionized Eu is represented by tetravalent Gd, the energy separation between the final-state Eu^{3+} and Eu^{2+} components should be given in first order by the energy difference between Gd^{4+} and Gd^{3+} for the fully relaxed state. Johansson[8] calculated this splitting as 7.8 eV, in excellent agreement with the present results. Herbst and Wilkins[9] using a renormalized-atom scheme obtained for the splitting of the Eu $3d$ core level a value of 9.6 eV, which is slightly larger than the splittings observed for the metallic Eu solids. The somewhat larger splitting found for Eu_2O_3 indicates the absence of final-state conduction-electron screening in this insulator. Since in metallic Eu^{3+} systems a larger screening shift is expected for the $4f^6$, as compared to the $4f^7$ configuration, the splitting should be reduced in metallic systems as compared to insulating solids.

Since the initial-state configuration of divalent Eu is $4f^7$ the XPS spectra of divalent Eu metal and to a less extent of $EuAl_2$ show the existence of a *shake-up* process characterized by a *decrease* of the $4f$ occupation number. In the trivalent Eu compounds studied ($EuPd_3$, $EuRh_6B_4$, Eu_2O_3), on the other hand, *shake-down* satellites are observed, which are due to an *increase* of the $4f$ occupation number.

The shake-down satellites observed for the trivalent Eu compounds may contain contributions from an initial-state surface-induced valence transition to the divalent state.[12] We have studied such a possibility by two methods, (i) by varying the electron take-off angle relative to the surface normal (which changes the effective electron escape depth) and (ii) by taking into account the different electron escape depths λ of the photoelectrons from $3d$- and $4d$-core levels (Fig. 2) (a ratio of $\lambda_{4d}/\lambda_{3d} \simeq 3$ can be expected for the kinetic energies resulting from excitation with Al $K\alpha$ x rays).[13] While on the basis of this analysis contributions from surface-induced valence transitions can be neglected for Eu_2O_3 and $EuRh_6B_4$ a possible contribution could not be excluded for $EuPd_3$. (A detailed analysis where both, a shake-up process in the divalent surface layer and a shake-down process in the trivalent bulk are considered, will be published elsewhere.) For the shake-up satellites observed for divalent Eu metal (and $EuAl_2$), however, such contributions due to a surface-induced valence change mechanism can be excluded, since the change in coordination at the surface would always favor the lower-valent state of the rare-earth ion.[14]

Both the shake-up and the shake-down processes can be consistently described within an extension of the KT model to f and d states. For simplicity let us consider a RE system with energetically degenerate f and d states (this situation is realized in an intermediate-valent system[15]). Then we have the following

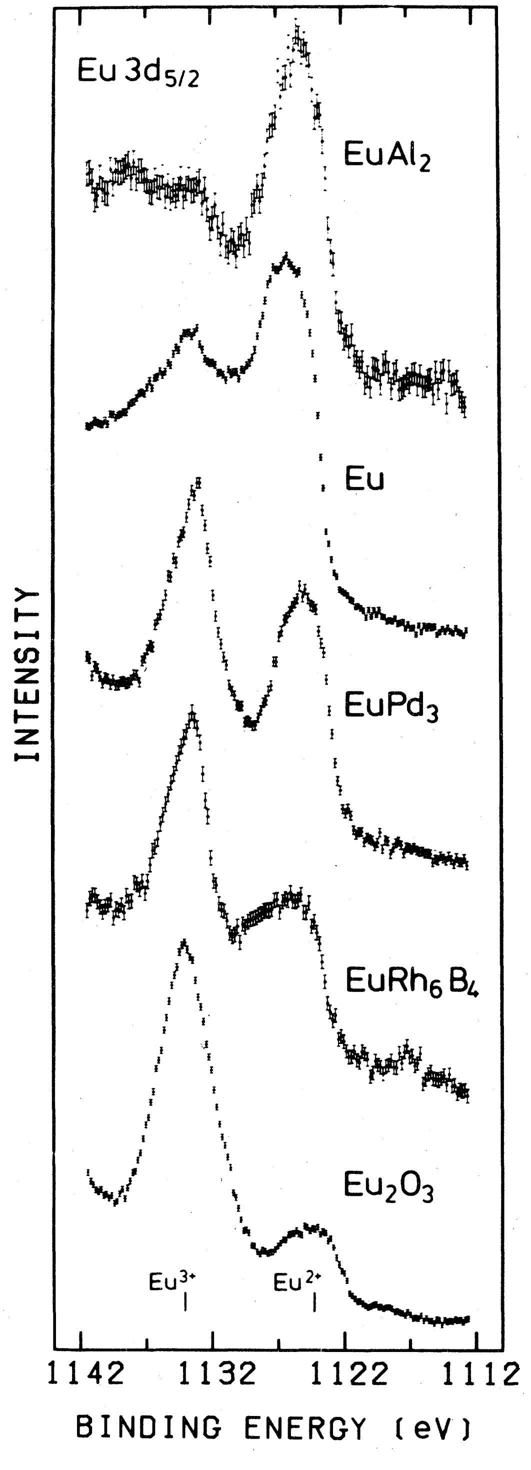

FIG. 1. XPS spectra of the Eu $3d_{5/2}$ region in $EuAl_2$, Eu metal (Ref. 19), $EuPd_3$, $EuRh_6B_4$, and Eu_2O_3, excited with Al $K\alpha$ x rays. The $K\alpha_{3,4}$ satellites were numerically removed. The structure in the $EuAl_2$ spectrum at a binding energy of 1138 eV is due to plasmon loss. The Eu_2O_3 spectrum shown was obtained with a pressed-powder sample.

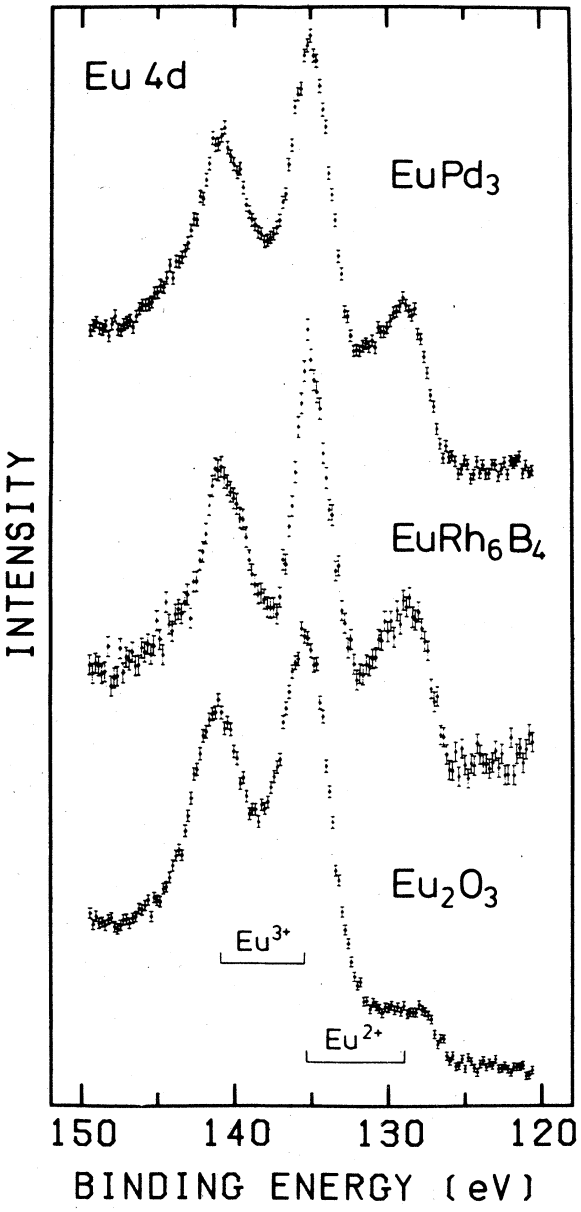

FIG. 2. XPS spectra of the Eu 4*d* region in $EuPd_3$, $EuRh_6B_4$, and Eu_2O_3 excited with Al $K\alpha$ x rays. The $K\alpha_{3,4}$ satellites were numerically removed. Note the similarity of these spectra of stable valent Eu^{3+} compounds with those presented in Ref. 20 for the mixed-valence compounds $EuRh_2$ and $EuRh_{2-x}Pt_x$.

possible initial-state configurations

$$R\,f^n(5d6s)^{m+1}, \qquad (1)$$

$$R\,f^{n+1}(5d6s)^m, \qquad (2)$$

where R denotes the Xe core, and n and m stand for f and d occupation numbers. Describing the PE process in the light of the KT model the potential of the photohole leads to a deformation of the local density of states, due to lowering of states relative to the Fermi energy. If an unoccupied state is pulled down below the Fermi level in the final state, a finite occupation probability depending on the *fds* hybridization, the local density of states, and the position of initial and final states relative to the Fermi energy will exist. A core-level photoionization of initial state (1) yields the following final states (neglecting extra-atomic relaxation)

$$R^+4f^n(5d6s)^{m+1}h_f+e^-, \qquad (3)$$

$$R^+4f^{n+1}(5d6s)^m h_d+e^-, \qquad (4)$$

where R^+ denotes the ionized core and h_f, h_d denote the f and d holes, respectively. Here, under the influence of the photohole, an initially unoccupied 4f state (h_f) is stabilized below the Fermi energy (3) and populated in Eq. (4), leaving behind a conduction electron hole h_d. The transition from Eqs. (3) to (4) corresponds to final-state screening accompanied by an increase in f occupation number. However, the transition from Eqs. (3) to (4) is not characterized by a simple recombination but by an equilibrium between the occupation of 4f and 5d states given by definite transition probabilities.

Let us now consider a core-level photoionization of initial state (2). Here a d state is assumed to be slightly above the Fermi energy. This state can now be pulled down by the increased core potential and is coupled with the corresponding 4f state in the same way as the unoccupied 4f state is coupled with the occupied d state in Eq. (1). Thus we should arrive at the same final states (3) and (4) with the same occupation probabilities. The transition from Eqs. (2) to (3) corresponds then to a final-state shake-up process accompanied by a decrease in 4f occupation number.

In the case of a stable configuration, the states (1) and (2) are separated by different KT parameters (hybridization, local density of states, etc.). Thus depending on the initial-state configurations (1) or (2) different transition probabilities to states (3) or (4) are expected. For both $4f^6$ and $4f^7$ initial states, however, the two final-state configurations (3) *and* (4) are expected and are indeed observed.

In the picture of Fuggle *et al.*[4] the peaks belonging to the $4f^6$ and $4f^7$ Eu configurations would be labeled as poorly screened and well-screened peaks. In the case of divalent Eu metal, however, this term is somewhat misleading, since the $4f^6$ final state in Eu metal (with both the 3d core hole and the hole in the 4f shell) may be better characterized as a two-hole final state. Then the connection of this shake-up phenomenon to the well-known Ni satellite[16] and the recently discussed two-hole final states in U compounds[17] is evident.

Let us finally consider a further unoccupied f state slightly above the Fermi level in the initial state.

Then, starting from state (2), an additional f-screened final state is possible

$$R^{+}4f^{n+2}(5d6s)^{m-1}, \tag{5}$$

leading to three energetically distinct final states (3), (4), and (5) in the PE spectrum. This situation may be present in Ce^{3+} compounds where such a threefold splitting has been observed in the $3d_{5/2}$ core-level spectra.[18] Then, the f^0 component, observed, e.g., in $CePd_3$ may be interpreted as being due to a final-state shake-up process accompanied by a decrease in f occupation number rather than being indicative for Ce^{4+} in the initial state.

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