Surface effects in Eu intermetallics: A resonant photoemission study

W. D. Schneider, C. Laubschat, and G. Kalkowski

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany

J. Haase and A. Puschmann

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Germany

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The Eu—transition-metal compounds $EuAg_5$, $EuRh_2$, $EuPt_5$, and $EuPd_5$ were studied by resonant $4d \rightarrow 4f$ photoemission techniques. In divalent $EuAg_5$, a surface core-level shift of the final-state $4f^6$ multiplet components of 0.75 eV is found. For the trivalent Eu compounds $EuPt_5$ and $EuPd_5$ as well as for the mixed-valence compound $EuRh_2$, a surface valence change to the lower-valence state is observed. For $EuPt_5$, an inhomogeneously mixed-valence surface is noticed, pointing to a strong coordination dependence of the surface valence transition. The energy position of the final-state $4f$ screening orbital is discussed on the basis of $4d$ photoemission and photoabsorption threshold energies.

INTRODUCTION

The stability of $4f$ configurations at the surface of rare-earth metals and compounds has attracted considerable interest in the past few years. After the pioneering photoemission work of Wertheim and Crecelius,[1] who first observed a divalent surface layer of Sm ions on top of trivalent Sm metal, a number of rare-earth compounds were found to undergo a valence change to the lower-valence state of the solid surface.[2-9] This phenomenon is caused by a decrease in cohesive energy due to the reduced coordination at the surface as compared to the bulk.[10] The model was able to account for the surface valence change of Sm metal and could be successfully applied for the rare-earth sulfides[11] and dialuminides.[8] Scarce information of surface valence changes existed so far concerning Eu compounds. The systems studied to date were $EuPd_2Si_2$,[3] the $EuPd_x$ intermetallics,[9] and an oxidation study of Eu metal.[12] On the other hand, such an effect is expected to occur for a number of Eu compounds if Miedema's semiempirical scheme (developed to calculate the stability of a compound in the bulk)[13] is extended to the surface of trivalent Eu intermetallics.[14] Therefore, recently, an x-ray photoemission (XPS) core-level study on a number of Eu—transition-metal compounds was carried out which revealed the existence of surface valence changes in trivalent $EuNi_5$, $EuRh_5$, $EuPd_5$, and $EuPt_5$.[14] However, deep-core-level spectroscopy has the intrinsic problem of the simultaneous appearance of final-state shake-down processes[15] and, moreover, a direct spectroscopic investigation of the $4f$ valence-band emission is masked by the overlapping d bands of the host transition metals, which have comparable photoionization cross sections at these energies.[16] Therefore, it was not possible to determine the extent of the surface valence change, i.e., questions on the completeness of such valence transitions and on the homogeneous or inhomogeneous valence mixing at the surface remained open.

The aim of the present work is to clarify these problems by circumventing the difficulties and pitfalls of core-level spectroscopy[17] through the application of synchrotron radiation at the Berlin Electron Storage Ring (BESSY). The resonant enhancement of the $4f$ states near the $4d$-$4f$ threshold energies[18,19] together with the favorable cross-section ratio of the $4f$ versus the transition-metal d states at these photon energies[20] were utilized to study and identify for the first time quantitatively different incomplete inhomogeneous valence changes at the surface of trivalent Eu intermetallics. Furthermore, a surface core-level shift in the divalent compound $EuAg_5$ is detected and compared with the results for other rare-earth compounds. Moreover, due to different resonance maxima for the $4d \rightarrow 4f$ excitations in Eu^{2+} and Eu^{3+} compounds, as observed for both direct photoemission and total electron yield spectra, a clear proof of the initial-state character of the surface valence change could be given. Furthermore, even in the total electron yield spectra, a distinction between bulk and surface states could be achieved.

EXPERIMENTAL

The samples of $EuPt_5$, $EuPd_5$, and $EuAg_5$ were prepared by arc melting and characterized by x-ray diffraction and Mössbauer spectroscopy.[14] The bulk valence was determined to be Eu^{2+} for $EuAg_5$ and Eu^{3+} for $EuPt_5$ and $EuPd_5$. The sample of the mixed-valence compound $EuRh_2$ is identical with the sample used in previous Mössbauer[21] and XPS studies.[22]

The photoemission measurements were performed at the Berlin Synchrotron radiation facility [Berliner Elektronenspeicherringgesellschaft für Synchrotron Strahlung mbH (BESSY)] with the SX-700 monochromator[23] with a photon flux of 3×10^{12} photons/sec $\Delta E\, A$ in the energy range $120 \leq h\nu \leq 150$ eV.[24] Photoemission spectra were recorded using a double-pass cylindrical mirror analyzer at ~0.5-eV resolution. At the $4d$-$4f$ resonance, typical count rates at the $4f^6$ emission peak were of the order of 10^4 counts/sec 0.1-eV channel. Total electron yield measurements[25] were carried out with a high-current channeltron in connection with a floating battery box and a

current amplifier. Typical output currents were of the order of 10^{-8} A.

Angle-integrated energy-distribution curves (EDC's) were measured at selected photon energies using the resonant enhancement of the $4f$ valence-band emission near the Eu $4d$ threshold.[18,26] The polycrystalline samples were scraped with a diamond file and studied *in situ* in a vacuum of 2×10^{-10} Torr. The surface conditions were checked by monitoring the O $2p$ signal at $h\nu = 20$ and 40 eV, respectively. No oxygen contamination could be detected as long as the scraping procedure was repeated every 30 min.

RESULTS AND DISCUSSION

In Fig. 1, EDC's are shown for EuPt$_5$ for $120 \leq h\nu \leq 300$ eV as a representative set of spectra for a trivalent Eu compound. The dominant contribution at $h\nu = 140$, 142, and 148 eV originates from electron emission to $4f^5$ and $4f^6$ final states[27] as indicated in the figure. At these energies the photoionization cross section is low for the transition-metal d states as compared to the $4f$ states.[20] We note the following observations: (i) at $h\nu = 132$ eV the $4f$ emission is totally suppressed, only the Pt $5d$ states are visible, (ii) at $h\nu = 140$ eV only a final-state $4f^6$ emission due to divalent Eu ions is resonantly enhanced, (iii) at $h\nu = 142$ eV the $4f^5$ emissions from trivalent Eu starts to contribute considerably to the $4f$ resonance, and (iv) from $h\nu = 148$ eV up to $h\nu = 300$ eV no considerable change in the Eu^{2+}/Eu^{3+} intensity ratio is observed. What is the reason for the $4f^6$ emission? Since Mössbauer spectroscopy has proved the bulk trivalent character of the Eu ions, we are faced with a surface valence change or a hypothetical final-state screening effect. The usual method, namely to quench the surface effect by oxidation,[4,28] is unsatisfying since oxidation alters considerably the geometric and electronic surface structure. In the case of the Eu compounds we get a direct proof for the initial-state character of the surface emission due to the different resonance behavior of Eu^{2+} and Eu^{3+} ions. Starting from the trivalent Eu-ion configuration

(1) $4d^{10}4f^6(5d\,6s)^3$,

we have at resonance

(2) $4d^9 4f^7 (5d\,6s)^3$,

where the $4f$ screening orbital becomes occupied directly in this excitation process. The normal Super—Coster-Kronig decay of this excited state leads to the configuration

(3) $4d^{10}4f^5(5d\,6s)^3$,

i.e., the trivalent photoemission signal. In order to obtain a $4f^6$ final state there remain two possibilities, another Auger decay via the $(5d\,6s)$ states

(4) $4f^{10}4f^6(5d\,6s)^2$

or by additional $4f$ screening of the trivalent state (3). However, both processes would be resonantly enhanced *together* with the $4f^5$ final-state photoemission signal from the trivalent Eu ion. Therefore, the *preceeding* onset of the $4f^6$ emission resonance clearly shows the initial-state character of the divalent Eu surface emission.

The compounds EuPd$_5$ and EuRh$_2$ show qualitatively similar spectra to the ones shown in Fig. 1, whereas in the divalent Eu compound EuAg$_5$, only the $4f^6$ resonance is present. The photoemission spectra of these compounds
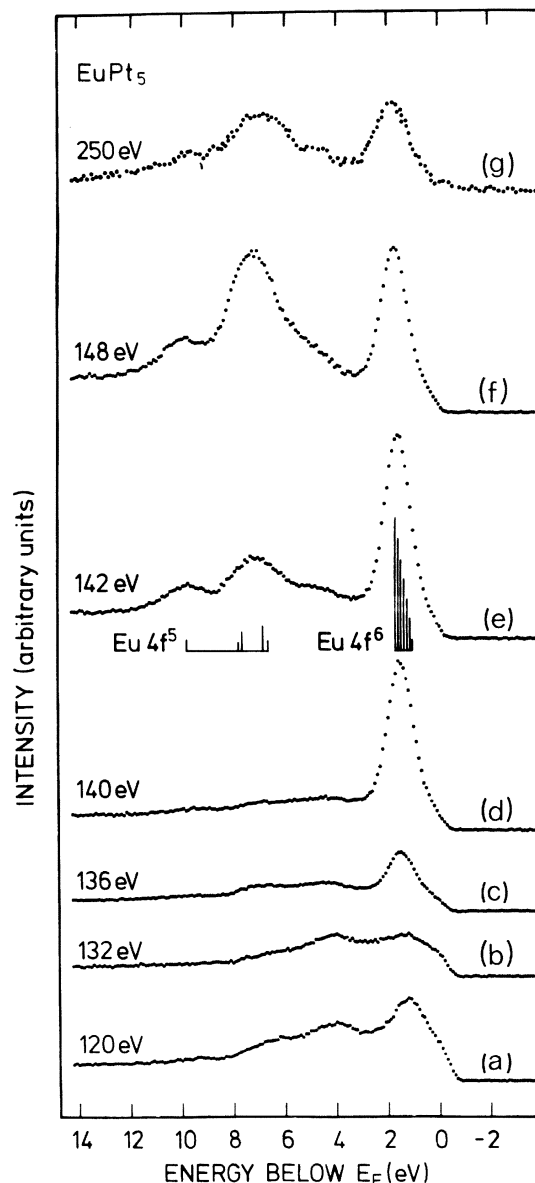

FIG. 1. Valence-band photoelectron energy-distribution curves (EDC's) of EuPt$_5$ excited at various photon energies between 120 and 250 eV. The spectra were normalized with respect to variations in the incident photon flux and electron analyzer efficiency. The relative intensities of the $4f^5$ and $4f^6$ emission varies with photon energy and a Fano minimum occurs around 132 eV. Note that the $4f^6$ emission precedes the $4f^5$ emission. The corresponding final-state multiplets are indicated.

taken at a photon energy of $h\nu = 148$ eV are shown in Fig. 2. The spectra are normalized to equal total $4f$ emission intensities (normalization to the beam current gives essentially the same result). We note a systematic increase of the divalent component in going from EuPt$_5$ to EuRh$_2$ and a strong increase in the linewidth for EuAg$_5$ pointing to the presence of a surface core-level shift in the latter case. In order to get quanitative information on the relative intensities of the bulk and surface spectral contributions, the final-state multiplets[29] were least-squares-
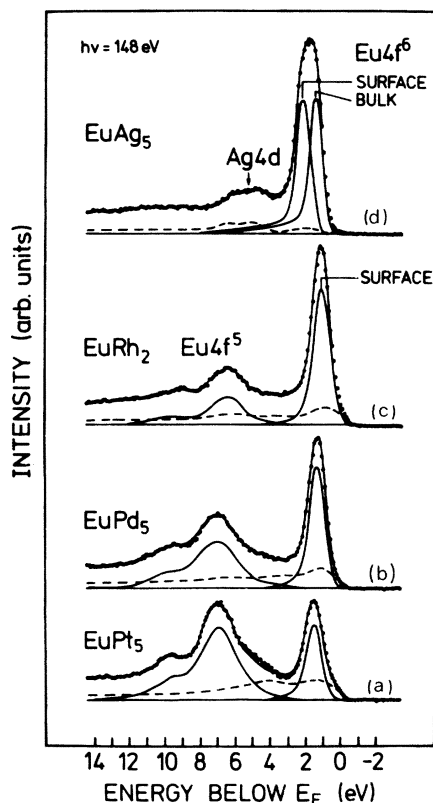
FIG. 2. EDC's of the valence bands of $EuAg_5$, $EuRh_2$, $EuPd_5$, and $EuPt_5$ taken at a photon energy of $h\nu = 148$ eV. The solid line following the data points represents the result of a least-squares-fit analysis (see text) with a superposition of two $4f^6$ final-state multiplets for $EuAg_5$, and $4f^5$ and $4f^6$ final-state multiplets for the other compounds originating from the bulk and the surface (solid curves). The dashed line represents the background of d-band states of the transition metals taken at $h\nu = 132$ eV. The spectra were normalized to equal $4f$ emission intensity. Note the different surface contributions in these compounds.

FIG. 3. Valence-band photoemission spectra of $EuAg_5$ at $h\nu = 120$ eV. The solid lines following the data points represents the result of a least-squares-fit analysis with a superposition of two $4f^6$ final-state multiplets originating from the bulk and the surface (solid curves). The dashed line denotes the integral background contribution.

analyzed with a Doniach-Sunjić line shape,[30] including an integral background (not shown in the figure) due to inelastically scattered electrons.

In order to extract the $4f$ intensity, the corresponding spectra at $h\nu = 132$ eV (where there is practically no $4f$ emission) were subtracted during the fit procedure. We have summarized the results of this analysis in Table I. For divalent $EuAg_5$, a surface core-level shift of 0.74 eV is measured. Figure 3 shows a clearer view of the surface effect at $h\nu = 120$ eV where the surface sensitivity is higher due to the lower kinetic energy of the photoelectrons. On
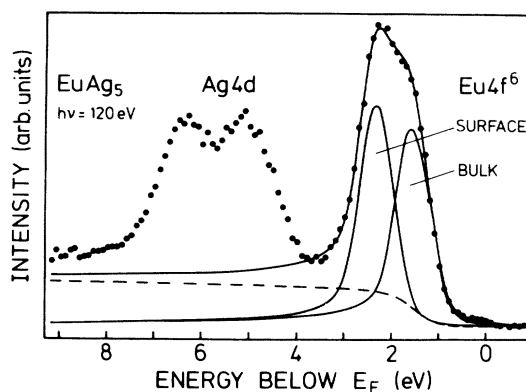
the other hand, the change in the relative photoionization cross sections for Ag, the $4d$, and the Eu $4f$ electrons, is noticeable. The value of the surface shift corresponds well to the systematics of core-level shifts for divalent rare-earth compounds and is near the one for EuPd.[9]

According to Table I the surface-to-bulk ratio in $EuAg_5$ corresponds to ~ 1. Taking this ratio as a "standard" for a divalent Eu monolayer at the surface of an Eu compound and assuming that the $4f^5$ components in the trivalent compounds contribute only to the bulk signal, we immediately see that 31% of the surface is divalent in $EuPt_5$ and 66% in $EuPd_5$. These numbers, however, have to be used with some caution since the ratio for the Eu^{2+}/Eu^{3+} photoionization cross section near the resonance may change. On the other hand, the spectra from $h\nu = 148$ eV up to photon energies of $h\nu = 300$ eV are very similar such that the error will not be too large to invalidate the observed trends. A more serious problem is the enhancement of the surface signal by segregation.[31] As compared to the trivalent compounds in the case of $EuAg_5$, such processes would be favored by the low formation enthalpy[13] and the large ionic radius of the divalent Eu ion. Therefore, the use of $EuAg_5$ as a standard for a completely divalent surface might be an overestimation. Nevertheless, the surface-to-bulk ratios in Table I should give a hint that even in $EuPd_5$ not more than one monolayer becomes divalent at the surface. In $EuPt_5$ it is evident that we encounter an incomplete surface valence transition. Since the measured energetic $4f$ positions of the lowest multiplet component (see Table I) are well below the Fermi energy, a homogeneous valence mixing of

TABLE I. Results of a least-squares analysis (see text) of the spectra shown in Fig. 2.

| Compound	Surface/bulk intensity ratio	Linewidth		Binding energy (E_F)	
		γ_S (eV)	γ_B (eV)	E_S (eV)	E_B (eV)
$EuAg_5$	0.98(3)	0.13(5)	0.13(5)	1.90(10)	1.15(10)
$EuRh_2$	1.55(3)	0.39(5)	0.76(10)	0.48(10)	5.79(10)
$EuPd_5$	0.66(2)	0.24(5)	1.04(10)	0.58(10)	6.17(10)
$EuPt_5$	0.31(1)	0.20(5)	0.85(10)	0.61(10)	5.92(10)

the surface has to be excluded. Thus a strong coordination dependence of the surface valence transition is proved. This finding is in excellent agreement with the stability of the $4f$ configurations in $EuPd_5$ and $EuPt_5$ as derived from the Miedema scheme in Ref. 14. A divalent surface is stabilized by only ~ 0.21 eV in $EuPt_5$, whereas in $EuPd_5$ it is stabilized by ~ 0.6 eV.

For the mixed-valence compound $EuRh_2$, a drastic increase in the Eu^{2+}/Eu^{3+} ratio as compared to $EuPd_5$ and $EuAg_5$ is observed. Indeed, a different ratio is expected since a divalent bulk contribution should occur at room temperature[22] which is nicely reflected in the increased linewidth γ (see Table I) not yet resolved.

This bulk contribution is reported to be 20% at room temperature and was derived from XPS measurements[22] without consideration of surface effects and should, therefore, be viewed with some reservation. If we take the surface-to-bulk ratio from $EuPd_5$ or $EuAg_5$ as a standard, we get from our measurements a value between 47% or 35% divalent character of this mixed-valence system. We want to point out that these values derived from the present measurements can be larger than the real bulk value due to surface relaxation effects. In the "second" and "third" layers[2,3] the interatomic distances may be enlarged leading to an enhancement of the divalent character of the surface region where most of the photoemission signal originates.

The measured surface-to-bulk ratios in the $4f$ emission provide the possibility to check the contributions of final-state shake-down processes to the divalent spectral components in deep-core-level spectroscopy.[14] The XPS spectra for $EuPd_5$ and $EuPt_5$ show for the $3d$ levels a ratio of 1.0 and 0.36, respectively, whereas we have a ratio of 0.66 and 0.31 for the $4f$ levels of these compounds (see Table I). In both cases the deep-core-level ratios are systematically higher than the ratios for direct $4f$ emission. On the basis of pure surface effects this finding is astonishing, since at ~ 148-eV kinetic energies the surface sensitivity should be higher than at 300 eV, the kinetic energies for the $AlK\alpha$ excited $3d$ core electron. This behavior would indicate the additional presence of final-state shake-down processes in deep-core-level spectroscopy. On the other hand, we must keep in mind, as discussed above, the uncertainty in the determination of the Eu^{2+}/Eu^{3+} intensity ratios, so that these numbers indicate a trend but do not allow a firm conclusion solely on the basis of the presented data.

Another more indirect method for the investigation of screening processes in XPS core-level ionization lies in the determination of the energetic position (relative to the Fermi energy) of the $4f$ screening orbital. As already mentioned above, the excitation of trivalent Eu at the $4d \rightarrow 4f$ resonance leads formally to the occupation of the $4f$ screening orbital (2) yielding the same final state as encountered in the direct photoionization of the $4d$ shell with $4f$ screening, i.e.,

$$4d^9 4f^7 (5d\,6s)^3 \ .$$
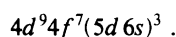
This state constitutes the final state of $4d$ photoionization of *divalent* Eu with $5d$ screening, the multiplet components of which can be directly inferred from $4d$ photoemission spectra of divalent Eu.[32,33] The correct position

E_s of the screening orbital relative to the Fermi energy is obtained if the energetically lowest multiplet component E_M (in our case ^7D) is shifted towards the Fermi energy by the value of the threshold energy E_{df} for the $4d \rightarrow 4f$ resonance

$$E_S = E_{df} - E_M \ ,$$

where the threshold energies are obtained from total electron yield measurements.

In Fig. 4 the results of these measurements in the $4d$ region of all Eu compounds studied here are shown. The structures between 132 and 140 eV point to the fact that the yield spectra of the trivalent compounds consist of a superposition of divalent and trivalent components which increase in analogy to the photoemission spectra in going from $EuPt_5$ to $EuRh_2$, whereas in $EuAg_5$ only the divalent final-state component is present.

This component corresponds in structure and position to the results for Eu metal,[12,34,35] whereas the constant—final-state yield spectra (CFS) of the Eu oxides show also a superposition of divalent and trivalent components.[12] In order to isolate the spectral structure of the trivalent component, the $EuAg_5$ spectrum was subtracted after proper normalization from the $EuPt_5$ yield spectrum.
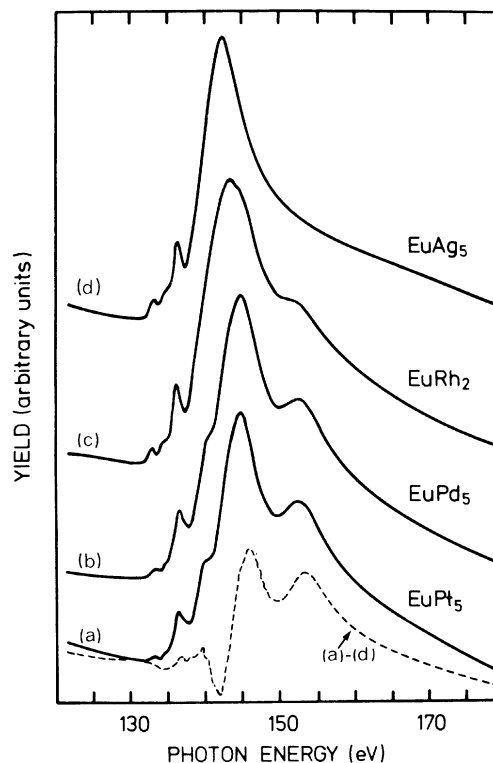

FIG. 4. Total photoelectric yield spectra from polycrystalline samples of $EuAg_5$, $EuRh_2$, $EuPd_5$, and $EuPt_5$ showing the $4d \rightarrow 4f$ absorption region. The dashed curve represents the result of a subtraction of a normalized $EuAg_5$ spectrum from the $EuPt_5$ spectrum in order to determine the divalent contribution in the trivalent compounds. Note that the maxima for the $4d^9 4f^7$ and $4d^9 4f^8$ final states are displaced by ~ 4 eV, enabling the observation of an increase in the divalent spectral character (from the bottom to the top of the figure.)

The result is indicated in Fig. 4 by the dashed line. We note an excellent agreement with corresponding constant—initial-state (CIS) spectra of Ref. 12, which are taken at the binding energy of the trivalent components. This superposition of divalent and trivalent final states in the yield spectra has the advantage of nearly independent observation of the divalent spectral contribution in the resonant photoemission spectra; however, this superposition makes it difficult to locate exactly the threshold for the onset of the trivalent emission on the photon energy scale. The difference spectrum shown in Fig. 4 in any case allows us to extract $E_{df} \geq 133$ eV. From the XPS photoemission spectrum[14] we have $E_M \cong 133-134$ eV and therefore

$$E_S \geq E_F \; .$$

This result deserves some comments since already in the ground state the unoccupied $4f$ level lies only ~ 0.5 eV above the Fermi energy[13] and therefore is not essentially lowered by the potential of the $4d$ core hole. On the basis of this finding it seems questionable that the $4f$ state can be lowered below the Fermi level under the influence of a $4d$ hole and can become a final-state screening orbital. On the other hand, one could argue that the population of the $4f$ screening orbital would lead to a local decrease of the conduction-electron concentration in the time scale of the photoemission, which in turn would cause a stabilization of the screening orbital below the Fermi energy. In principle, however, an unoccupied $4f$ state above the Fermi level may also be populated by shake-up-type scattering of conduction electrons into this state.[36]

It is interesting to compare this result with the results for trivalent Sm in Sm metal and SmB$_6$ (Ref. 28), where a lowering of $4f$ states with respect to a fictive, final state [which was composed out of XPS and bremsstrahlungs isochromat (BIS) final states] was deduced. If we apply our method for the determination of the energetic position of the $4f$ state relative to the Fermi level to the case of trivalent Sm metal, we obtain with $E_{df} = 125.5$ eV (Ref. 28) and $E_M \approx 130$ eV (Ref. 32) a value of $E_S \sim -4.5$ eV, which is clearly below the Fermi level. Since in the ground state similar to trivalent Eu the unoccupied $4f$ level resides near above the Fermi energy,[10] we obtain, in contrast to Eu, a lowering of this state by about 5 eV. The reason for this discrepancy may be explained by multiplet effects. The $4f$ screening orbital is a highly correlated state which is not allowed to be shifted in a simple one-electron picture. The lowered state is the energetically

lowest term of a $4d^9 4f^n$ multiplet, whereas the BIS state (used in Ref. 28) represents the lowest term of the $4d^{10} 4f^n$ multiplet. Both multiplets show totally different couplings,[32,33,37] the splittings of which vary by several eV. Thus the "lowering" of the $4f$ screening states cannot be compared directly for different occupation numbers n. To summarize this section, even with resonant photoemission techniques it is not possible to determine unambiguously the role of final-state effects in deep-core-level spectroscopy of Eu compounds.

SUMMARY

We have studied the intermetallic compounds EuAg$_5$, EuPt$_5$, EuPd$_5$, and EuRh$_2$ with resonant photoemission techniques at the $4d \rightarrow 4f$ threshold. In divalent EuAg$_5$, a surface shift of 0.75 eV was detected which fits well into the general picture of core-level shifts in rare-earth compounds. For the trivalent Eu compounds EuPt$_5$ and EuPd$_5$ as well as for the mixed-valence compound EuRh$_2$, a surface valence change to the lower-valence state was observed. For EuPt$_5$ we noticed an inhomogeneously mixed-valence surface pointing to the strong coordination dependence of this effect. A comparison of surface-to-bulk intensity ratios found in the $4f$ spectra with those reported for $3d$ core-level spectra indicated a contribution of final-state screening in the latter case. Moreover, we showed that it is possible to use total electron yield to study surface valence transitions in Eu compounds since the resonance maxima for $4f^7$ and $4f^8$ final states, i.e., the bulk and surface contributions, differ by ~ 4 eV. This specific resonance behavior allowed a direct proof of the initial-state character of the observed surface valence changes. Finally, on the basis of a comparison between $4d$ photoemission and photoabsorption thresholds, it was shown that the $4f$ screening orbital in the photoionization of trivalent Eu compounds is stabilized at or near above the Fermi energy.

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