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Final-state effects and surface valence in Eu—transition-metal compounds

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A systematic x-ray photoemission study of Eu $3d$ and Eu $4d$ core levels in the Eu—transition-metal compounds $EuRh_5$, $EuNi_5$, $EuPd_5$, $EuPt_5$, $EuCu_5$ and $EuAg_5$ is presented. The spectra in the divalent and trivalent compounds exhibit splittings into two components, caused by the occurrence of $4f^6$ and $4f^7$ configurations. For the divalent compounds $EuCu_5$ and $EuAg_5$, this effect is due to final-state shakeup. For the trivalent compounds, the presence of both configurations is discussed in terms of both initial- and final-state effects. An estimate of the $4f$-configurational stability at the surface of the Eu^{3+} intermetallics indicates surface valence transition of the Eu ions to the lower valent state in these compounds. Experimental evidence for this behavior is given.

INTRODUCTION

Rare-earth (RE) ions are trivalent in most of their compounds. Some of the rare-earth elements, however, are found to be divalent or tetravalent in a solid. This property of the rare-earth ions, namely, to form different valences depending on the type and concentrations of the other components of the compound, leads in some cases to the interesting phenomenon of valence instabilities, i.e., mixed valences, valence fluctuations, and surface valence transitions.[1] These ground-state properties are closely related to final-state effects in photoemission core-level spectroscopy where a change in the $4f$-occupation number is induced by the creation of the photohole.[2] Such phenomena were frequently encountered in light rare-earth systems and were interpreted as shakedown final-state screening processes.[3–5] Here, in the light of the equivalent core argument, unoccupied $4f$ states are lowered by the potential of the photohole and are occupied by valence electrons,[6,7] leading to an increase of the $4f$-occupation number. With increasing atomic number and thereby increasing $4f$ localization the probability of the screening mechanism decreases and approaches zero in Sm systems.[8] In Eu compounds, however, due to the energetic degeneracy of the Eu $4f^6 5d^1$ and Eu $4f^7 5d^0$ configurations, both configurations are observed in the final-state independent of the initial-state valence.[9] Here, in addition to the shakedown process present in Eu^{3+} compounds, the reverse process, a shakeup (where a localized $4f$ electron is scattered into the conduction band, leading to a decrease of the $4f$-occupation number) was discovered in Eu^{2+} compounds.[9] As can be inferred from the intensity variations of the Eu^{2+} and Eu^{3+} final-state components in various compounds, the probability for both shakeup and shakedown processes is strongly correlated with the chemical environment of the rare-earth ions.[10] In the ground state the valence of Eu, i.e., the $4f$-configurational stability, in intermetallic compounds can be related within a semiempirical model[11] to the density of states,[12] the concentration, and the chemical potential of the other component.

The aim of the present photoemission study was (using Miedema's results for the stability of rare-earth intermetallic compounds) to investigate if deep-core-level spectroscopy can answer the question to what extent final-state effects (shakeup and shakedown) interfere with initial-state processes like valence transitions[13] at the surface of trivalent rare-earth compounds. In order to clarify this question we have chosen transition-metal compounds EuM_5 with $M =$ Rh, Ni, Pd, Pt, Cu, and Ag since in these compounds the Eu ion in the bulk possesses a stable valence in the ground state (as determined by Mössbauer spectroscopy). Eu is found to be trivalent in the late transition metals with a high density of d states at the Fermi energy and divalent in the noble-metal compounds with a broad s band. Moreover, $EuNi_5$, $EuCu_5$, and $EuAg_5$ belong to the class of Haucke compounds with the $CaCu_5$ structure which are of technological interest as hydrogen-storage materials.[14]

EXPERIMENTAL

The samples of the EuM_5 compounds were prepared by arc melting in reduced Ar atmosphere and tempered for one week in vacuum at 650 °C. The Eu content differed from the nominal value of 16.7 at. % by no more than 1 at. % in all cases. The samples were characterized by x-ray-diffraction and Mössbauer spectroscopy.

X-ray-diffraction patterns were recorded with a Debye-Scherrer camera and a proportional counter using the Cu $K\alpha$ radiation. $EuNi_5$,[15] $EuCu_5$,[16] and $EuAg_5$[17] show the well-known $CaCu_5$ patterns whereas $EuPt_5$ has the $SmPt_5$ structure.[18] In the case of $EuPd_5$ it is known from the study of the Eu-Pd phase diagram[19] that it is not possible to prepare a single-phase compound with the composition $EuPd_5$. The Mössbauer spectrum of our sample shows in agreement with earlier work[20] that the alloy contains mainly $EuPd_5$ with an admixture of $EuPd_3$ in our sample of approximately 20 at. %. This admixture can be identified in the x-ray pattern by the four most intense lines of $EuPd_3$. After subtracting the additional $EuPd_3$ lines from the $EuPd_5$ pattern we agree with Ref. 19 that it is not a $CaCu_5$ structure and suggest instead the $SmPt_5$ structure. From the similarity of the $EuRh_5$ with the

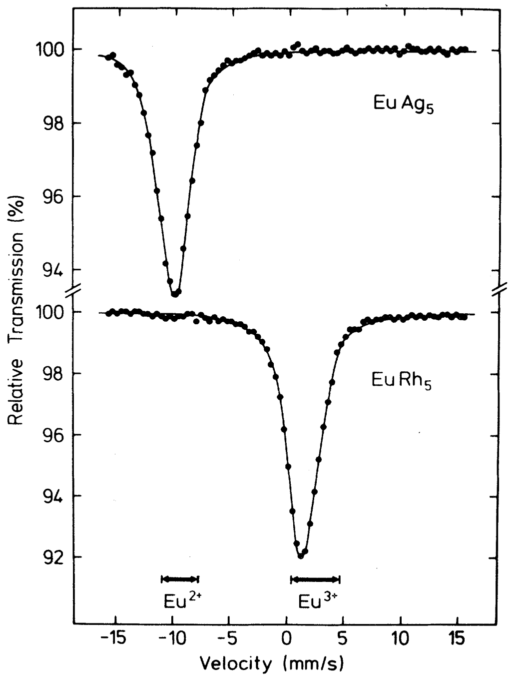

FIG. 1. Mössbauer transmission spectra of $EuRh_5$ and $EuAg_5$ at ambient temperature using the 21.5-keV transition of ^{151}Eu recorded with a $^{151}SmF_3$ source. Arrows indicate the range of isomer shifts for Eu^{2+} and Eu^{3+} resonances in metals, respectively.

$EuPt_5$ patterns we suggest for $EuRh_5$ the $SmPt_5$ structure as well.

Mössbauer transmission spectra were recorded with a constant-acceleration spectrometer using the 21.5-keV radiation of ^{151}Eu from a $^{151}SmF_3$ single-line source. All Mössbauer spectra show resonances with small quadrupole interactions due to the non-cubic-lattice structure and isomer shifts corresponding to Eu^{2+} ($EuCu_5$ and $EuAg_5$) or Eu^{3+} ($EuRh_5$, $EuNi_5$, $EuPt_5$, and $EuPd_5$).[21] Figure 1 shows typical spectra of $EuRh_5$ and $EuAg_5$ as representatives for an Eu^{3+} and Eu^{2+} resonance, respectively. The spectra of $EuPd_5$,[20] $EuCu_5$,[16] and $EuPt_5$ (Ref. 22) are in excellent agreement with earlier work. With the exception of $EuPd_5$ (see above) the Mössbauer spectra prove the samples to be single phase with an accuracy of approximately 2%.

The x-ray photoelectron spectroscopy (XPS) measurements were performed with a VG-ESCA-3 spectrometer with a total resolution of $\cong 1$ 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).

In order to perform a quantitative analysis it was necessary to determine the intensities of the divalent and trivalent final-state components in the photoemission spectra. Because of the coupling of the photohole with the open 4f subshell the Eu core-level spectra contain, apart from the simple spin-orbit splitting, a complicated multiplet structure[23] which could not be resolved with the present spectrometer but which influences the line shape directly. Since we were mainly concerned with the intensities of the spin-orbit-split components, an experimentally derived line shape was deduced in the following way: The Eu4d line shape of the Eu^{2+} component was approximated by the Eu 4d spectrum of the compound $EuAg_5$ by subtracting an integral background due to inelastic scattering of the electrons on their way through the sample and by considering a weak doublet corresponding to the Eu^{3+} component. Within this line shape it was possible to obtain the line shape of the Eu^{3+} component in the spectrum of $EuPd_5$. In the case of the Eu 3d levels the spin-orbit interaction is large compared to the multiplet splitting.[23] Therefore, the much simpler shape of the Eu $3d_{5/2}$ components could be directly determined for both components on the basis of the $EuPd_5$ spectra.

These empirically determined line shapes superimposed by a linear and an integral background were used for all spectra in a least-squares-fitting procedure in order to obtain the relative intensities of the Eu^{2+} and Eu^{3+} final-state components. The error which is introduced by this approximation can be estimated by varying the line shapes within tolerable limits and comparing the resulting intensities. This procedure yields for the ratios of the derived relative intensities an error of about 10%.

RESULTS AND DISCUSSION

XPS spectra of the Eu $3d_{5/2}$ core-level region are shown in Fig. 2 for the five studied Eu solids. Note that in the case of the compound $EuAg_5$ a spectrum of the Eu $3d_{3/2}$ region is shown since the $3d_{5/2}$ region is superimposed by an Ag Auger emission. XPS spectra of the Eu 4d region are shown in Fig. 3 for the same compounds. The spectra are arranged in the scheme of the Periodic Table in order to facilitate the recognition of systematic trends. It is striking that for both Eu^{2+} and Eu^{3+} systems the Eu $3d_{5/2\,(3/2)}$ line is split into two components with varying relative intensities in spite of the fact that in all compounds an integral valence was present in the ground state. The contribution of the divalent final-state component increases if one proceeds in the period of the Periodic Table with respect to the compound component and decreases if one descends within the group. This effect is present to a lesser extent in the 4d spectra as well.

Crecelius *et al.*[24] and Herbst *et al.*[25] have shown that due to the stability of the half-filled 4f shell in Eu^{2+} the $4f^7$ and the $4f^8$ 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.[9] A further confirmation for the correctness of this identification is given by the magnitude of the observed splittings. With the use of 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[26,27] calculated this splitting as 8.6 eV, in excel-

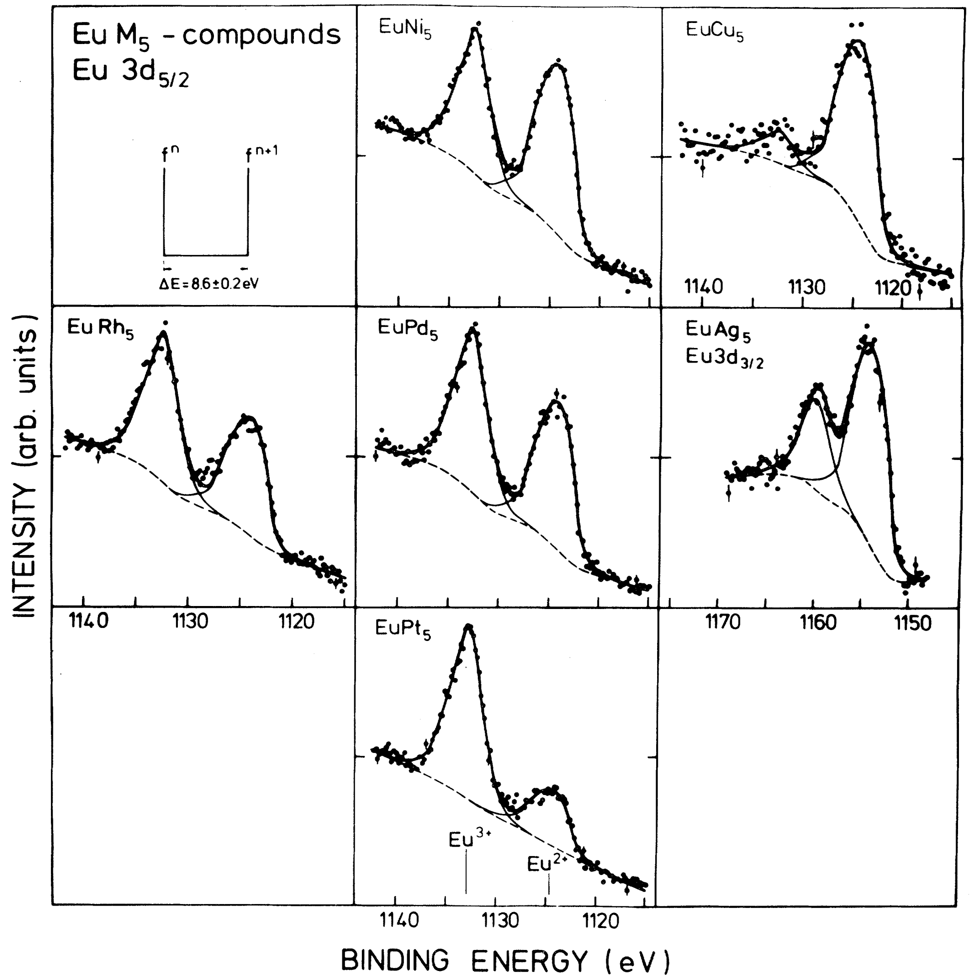

FIG. 2. XPS spectra of the Eu $3d_{5/2}$ region in $EuRh_5$, $EuNi_5$, $EuPd_5$, $EuPt_5$, $EuAg_5$ ($3d_{3/2}$), and $EuCu_5$, excited with Al $K\alpha$ x rays. The $K\alpha_{3,4}$ satellites were numerically removed. Thick solid curve represents the result of a least-squares fit (see text), the Eu^{2+} and Eu^{3+} components are indicated by thin solid curves, and the integral background is denoted by a dashed curve.

lent agreement with the present results. Herbst and Wilkins[28] 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 compounds (8.6 ± 0.2 eV). It is interesting to note that there are differences in the $3d_{5/2}$-$3d_{3/2}$ splittings of ~ 4 eV (see the $EuAg_5$ $3d_{3/2}$ spectrum in Fig. 2) which are caused by the different magnitude of the spin-orbit splitting for divalent and trivalent Eu ions.[27,28]

The appearance of divalent and trivalent components can be principally caused by an initial-state or a final-state property (shakeup or shakedown). If the origin of the observed structures is due to an initial-state process the effect must be restricted to the surface of the sample since otherwise Mössbauer spectroscopy would have detected mixed-valence behavior. Thus, in this case we encounter a surface contamination or a surface valence transition.

Surface contamination can be caused by oxygen leading to divalent EuO or trivalent Eu_2O_3. The measurement conditions, however, allow at most for 0.05% of a monolayer of oxygen on the sample surfaces. Consequently, contamination cannot be responsible for the observed effects in the spectra. A surface valence transition caused by the change in crystal symmetry at the surface (volume effect and change in the electronic density of states) is expected only for the trivalent Eu compounds, since the change in coordination at the surface would always favor the lower-valent state of the RE ion.[29] As a matter of fact, the Eu-rich compounds EuM and EuM_2 with the considered transition metals are all divalent, making a divalent Eu surface layer on top of a trivalent bulk layer in the EuM_5 system likely. In Sm metal and a few other cases such an effect of surface valence changes of RE atoms has been observed.[13,30–34]

In order to discuss more quantitatively such a possibility for the trivalent EuM_5 compounds we try (on the basis of Miedema's scheme[11]) to get an estimate for the $4f$-configurational stability at the surface of these systems. Let us consider in analogy to Johansson[29] the following cycle. In the first step we decompose the compound into

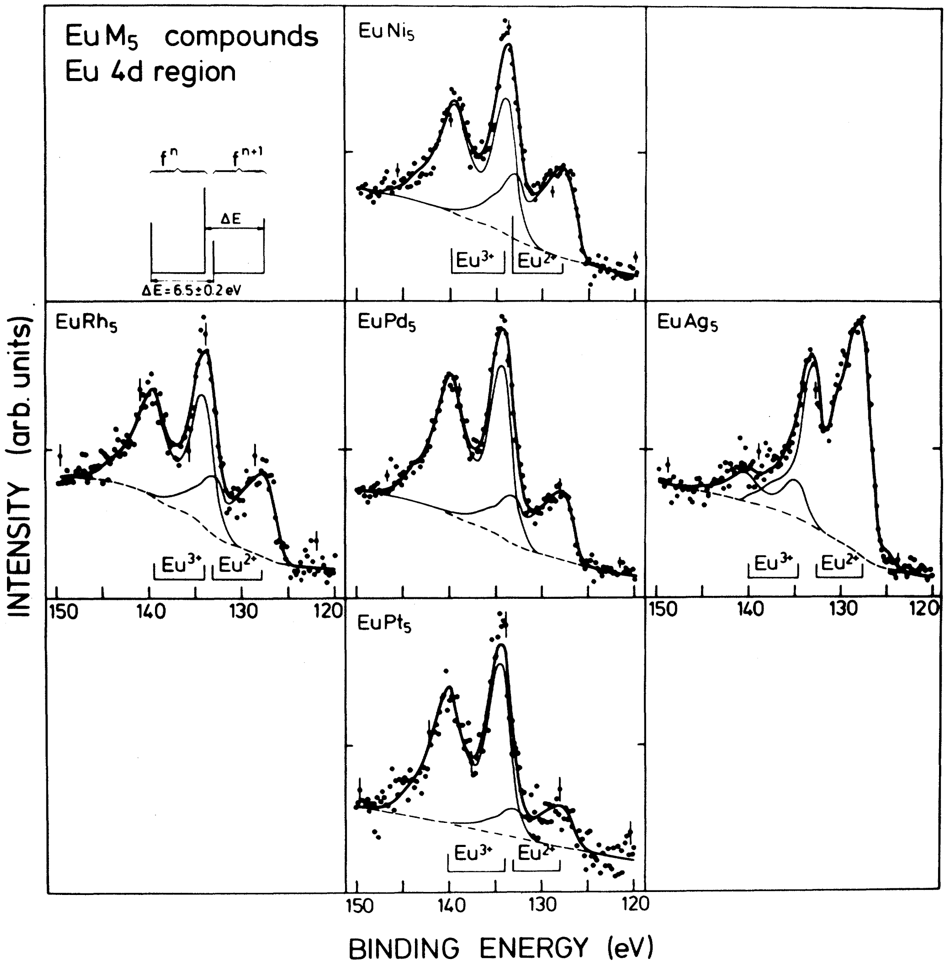

FIG. 3. XPS spectra of the Eu 4d region in EuRh$_5$, EuNi$_5$, EuPd$_5$, EuPt$_5$, and EuAg$_5$, excited with Al$K\alpha$ x rays. The $K\alpha_{3,4}$ satellites were numerically removed. Meaning of the curves is the same as in Fig. 2.

its elements where we have to put in the formation energy ΔH^{3+} and gain an entropy term ΔS_{bulk},

$$\text{(i)}\quad \Delta G^{3+}=\Delta H^{3+}_{\text{bulk}}-\Delta S_{\text{bulk}}\ .$$

Now we bring the atoms in the pure elements from the bulk to the surface where we have to invest the proper surface energies U^{3+}_{Eu} and U_M, respectively,

$$\text{(ii)}\quad \Delta G^{3+}=\Delta H^{3+}_{\text{bulk}}-\Delta S_{\text{bulk}}+U^{3+}_{\text{Eu}}+U_M\ .$$

Finally, we put together the atoms at the surface back to the original compound, gain a surface formation enthalpy $-\Delta H^{3+}_{\text{surf}}$, and lose an entropy term ΔS_{surf},

$$\text{(iii)}\quad \Delta G^{3+}=\Delta H^{3+}_{\text{bulk}}-\Delta S_{\text{bulk}}+U^{3+}_{\text{Eu}}+U_M-\Delta H^{3+}_{\text{surf}}+\Delta S_{\text{surf}}\ .$$

In order to obtain a divalent surface we have to convert Eu^{3+} in the bulk to Eu^{2+} where we gain 23 kcal/g-at.[11] Introducing this value in (ii) and (iii) and replacing U^{3+}_{Eu} and $\Delta H^{3+}_{\text{surf}}$ by the corresponding divalent quantities we have

$$\text{(iv)}\quad \Delta G^{2+}=\Delta H^{3+}_{\text{bulk}}-\Delta S_{\text{bulk}}-23\ \text{kcal}+U^{2+}_{\text{Eu}}+U_M-\Delta H^{2+}_{\text{surf}}+\Delta S_{\text{surf}}\ .$$

The difference (iv) — (iii) gives

$$\Delta G=\Delta G^{2+}-\Delta G^{3+}=-23\ \text{kcal}+(U^{2+}_{\text{Eu}}-U^{3+}_{\text{Eu}})-(\Delta H^{2+}_{\text{surf}}-\Delta H^{3+}_{\text{surf}})\ ,$$

where a negative value of ΔG constitutes the condition for a surface valence transition. With $(U^{2+}_{\text{Eu}}-U^{3+}_{\text{Eu}})\approx 12$ kcal (Ref. 29) we get

$$\Delta G=-35\ \text{kcal}-\Delta H_{\text{surf}}\ ,$$

with $\Delta H_{\text{surf}}=\Delta H^{2+}_{\text{surf}}-\Delta H^{3+}_{\text{surf}}$. It is difficult to obtain an estimate for this quantity since the symmetry at the surface is distorted and therefore Miedema's scheme is not directly applicable. We note, however, that the decrease in coordination number at the surface leads to an increase of the effective Eu concentration and on the other hand to a

TABLE I. Difference between the heat of formation of intermetallic compounds of divalent and trivalent europium metal ΔH_{bulk} (Ref. 11) and the stabilization energy for a divalent surface ΔG.

Compound	ΔH_{bulk} (kcal/g-at. Eu)	ΔG^{a} (kcal/g-at. Eu)
$EuNi_5$	-31	-4
$EuRh_5$	-30^{a}	-5
$EuPd_5$	-21	-14
$EuPt_5$	-31	-4

[a] Calculated in this work.

decrease of the contact areas of neighboring Wigner-Seitz cells. Both effects would lead to a reduction in the absolute value of ΔH_{bulk} in Miedema's scheme. Therefore we assume that ΔH_{surf} in the present case is lower than the respective bulk value leading to the following inequality:

$$\Delta G \leq -35 - \Delta H_{\text{bulk}} \; .$$

Table I lists the result for the trivalent compounds where the ΔH_{bulk} values are taken from Miedema's calculations.[11] It is obvious from this table that ΔG is negative for all compounds suggesting a surface valence transition to the lower-valent state for all trivalent EuM_5 compounds.

In order to prove the existence of a divalent surface layer with photoemission techniques we use two methods. If one assumes a simple extinction law $\exp[-D/\lambda(E)\cos\theta]$ (Ref. 35) for the scattering of the photoelectrons as a function of the traversed layer thickness D where λ denotes the mean free path of the electrons, E is the kinetic energy, and θ describes the polar angle of electron emission, then the contributions I_s of a surface layer with thickness D to the photoelectron spectrum is given by

$$I_s = 1 - \exp[-D/\lambda(E)\cos\theta] \; . \tag{1}$$

If the contribution I_s is identified with the divalent component I_{2+} observed in the spectrum, then from the variation of this quantity as a function of θ or $\lambda(E)$ the surface-layer thickness D is obtained directly. A variation of the polar angle θ is identical with a variation of electron angle between the sample-surface normal and the analyzer slit of the spectrometer. Here it is not appropriate, however, to attempt to vary the takeoff angle because the sample surfaces are rough. Therefore, it is more reasonable to use the energy dependence of the mean free path for such an analysis. The absolute values of the mean free path as a function of the material under consideration and the kinetic energy of the photoelectrons are still a matter of investigation; however, the basic trend in the high-energy region is well understood theoretically. Following calculations of Penn[36] the ratio of λ(1300 eV) to λ(300 eV), corresponding to the mean free paths of Eu $4d$ and Eu $3d$ photoelectrons, respectively (excited with Al $K\alpha$ radiation), for most transition metals amounts to

$$\frac{\lambda(1300\ \text{eV})}{\lambda(300\ \text{eV})} = \frac{\lambda(4d)}{\lambda(3d)} \approx 2.8 \; .$$

This value can now serve for a comparison with an experimentally derived λ ratio on the basis of Eq. (1) . If we define the following ratios for the spectra of the $3d$ and $4d$ region (with $n = 3,4$):

$$V(nd) = I_{2+}/I_{3+} = I_s/(1-I_s) = \exp[D/\lambda(nd)\cos\theta]^{-1} \; ,$$

we have for the experimentally determined λ ratio,

$$\lambda(4d)/\lambda(3d) = \ln[1+V(3d)]/\ln[1+V(4d)] \; ,$$

where the $\cos\theta$ term vanishes.[35] We have listed these ratios together with the intensity ratios $V(3d)$ and $V(4d)$ in Table II. The comparison with the theoretically expected λ ratio of ≈ 2.8 shows immediately that with the exception of $EuPd_5$ the experimentally determined values in column 3 of Table II are significantly lower. A possible explanation of this finding may be an incomplete divalent surface layer on top of a trivalent bulk, an issue already discussed in the case of Sm metal.[13] The small stabilization energies ΔG (see Table I) for $EuNi_5$, $EuPt_5$, and $EuRh_5$ would favor such an interpretation. However, the interpretation of the spectra on the basis of an incomplete divalent surface layer alone is unsatisfying for the following reasons. The thickness of the divalent surface layer should be mainly determined by the diameter of the divalent Eu ion and therefore should be of comparable dimensions in all samples. From the above calculation of ΔG and from experiments[30] $EuPd_5$ is expected to show a complete divalent surface layer. Then $EuNi_5$, $EuPt_5$, and $EuRh_5$ should show at least the same amount of divalent character. A comparison of the spectra in Fig. 2 and of the results in Table II, however, indicates that this statement fails for $EuNi_5$ which clearly shows the strongest divalent component. This discrepancy could be explained by surface segregation[37] of Eu ions leading to divalent Eu islands at the surface. An argument which may support such a possibility lies in the smallness of the Ni atoms and in the low-formation energy of this compound[11] which would favor a decomposition, i.e., surface segregation. We cannot completely rule out this effect, however, since we are dealing with intermetallic compounds and not with alloys we believe that the contribution of surface segregation to the Eu^{2+} component is only of minor importance.

Another possibility not discussed so far is the presence of final-state effects. As can be seen in the divalent compounds where the appearance of the trivalent component cannot be caused by a surface effect, corresponding processes in the trivalent spectra can certainly not be neglected. These final-state effects have their origin in a Coulomb interaction of the created photohole and the emitted photoelectron with the electronic system and may lead to a change in the $4f$-electron occupation number and consequently to a change of the nominal valence. In the shakedown process an unoccupied initial $4f$ state is lowered by the potential of the photohole and becomes occupied by a conduction electron (final-state screening). This process is well known in the photoemission spectra of light RE systems and has been used, too, in the interpreta-

TABLE II. Experimentally determined intensity ratios and the derived mean-free-path ratios.

Compound	Intensity ratio $V(3d)$	Intensity ratio $V(4d)$	Derived mean-free-path ratio $\lambda(4d)/\lambda(3d)$	$V(3d)/V(4d)$
$EuNi_5$	1.34 ± 0.13	0.69 ± 0.07	1.62 ± 0.25	1.94 ± 0.4
$EuPd_5$	1.01 ± 0.10	0.40 ± 0.04	2.07 ± 0.35	2.53 ± 0.5
$EuPt_5$	0.36 ± 0.04	0.24 ± 0.03	1.43 ± 0.20	1.50 ± 0.3
$EuRh_5$	0.89 ± 0.09	0.65 ± 0.07	1.27 ± 0.20	1.37 ± 0.3
$EuAg_5$	2.46 ± 0.25	5.9		0.41
$EuCu_5$	6.33 ± 0.7			

tion of the spectra of Eu^{3+} solids.[9] A formal reversion of this process is given by a shakeup excitation, where similar to an autoionization effect a localized $4f$ electron is scattered into the conduction band. Such a process which is well known from atomic and molecular spectroscopy has been postulated for the core-level ionization of metallic Eu (Ref. 9) and should be considered for the trivalent components in $EuCu_5$ and $EuAg_5$. The intensity of the observed final-state effects depends on several parameters, i.e., the local density of states and the hybridization of the $4f$ levels with the other valence- and conduction-electron states. Therefore, the observed systematic decrease of the divalent component in the trivalent compounds from $EuNi_5$ to $EuPt_5$ may reflect the change in the electronic properties of the host metal. However, the total 2^+ intensity cannot be caused by final-state effects. Because of the different radial extent of the $3d$ and $4d$ wave functions different final-state-effect intensities are expected for $3d$ and $4d$ photoionization. Since this difference in the case of highly localized core levels depends only on an atomic property this final-state effect should be independent of the metallic matrix of the system. If we identify the *entire* observed effect in the spectra with a final-state process then the λ ratios should be 1 and the ratio of ratio numbers $V(3d)/V(4d)$ should be constant. As can be seen from column 4 of Table II this is not the case. Consequently, for the trivalent compounds a mixture of initial- and final-state effects is present the relative contributions of which cannot be extracted on the basis of core-level spectra alone.

A possibility to clarify some of these open questions constitutes photoenergy-dependent measurements of the valence band of these Eu intermetallics, which should enable (using the fact that a suppression of d emission in the Cooper minimum[30,31] is present) a direct observation of $4f$ emission from divalent europium. Since the $4f$ emission is not strongly influenced by final-state effects[38] through a comparison with the present measurements a quantitative separation between initial- and final-state effects could be feasible.

SUMMARY

We have investigated EuM_5 transition-metal compounds by means of deep-core-level photoelectron spectroscopy. The observed Eu $3d$ and Eu $4d$ spectra of divalent and trivalent Eu compounds exhibit splittings into two components caused by the occurrence of $4f^6$ and $4f^7$ configurations. For the divalent compounds the effect can be attributed to a final-state shakeup. In the case of the trivalent compounds the presence of both configurations can be due to both initial-state and final-state effects. An estimate of the $4f$-configurational stability of the surface of the trivalent compounds indicates surface valence transitions in all trivalent EuM_5 compounds. Experimental proof of this expectation is complicated by the possible cooperative action of incomplete surface valence transitions, surface segregation, and final-state shakedown processes. Since we have shown that the final-state effect cannot be responsible alone for the total divalent intensities the existence of divalent Eu ions at the surface of the trivalent Eu compounds is proved. Thus the trivalent EuM_5 compounds belong to the interesting class of materials with a surface layer of magnetic europium atoms on top of a nonmagnetic bulk.[30]

These results raise severe questions in connection with the investigation of mixed-valent materials by deep-core-level spectroscopy. Evidently replicate core levels in RE systems cannot serve as a fingerprint for intermediate-valence behavior. However, the presence of such features indicates that the electronic system (due to $4f$-electron—conduction-electron hybridization[5]) is close to an instability. The question remains to what extent final-state (shakeup and shakedown), initial-state (surface valence change), or a complicated mixture of both effects do contribute. Synchrotron-radiation experiments may give the answer in the near future.

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

[2] G. K. Wertheim and M. Campagna, Solid State Commun. 26, 553 (1978).

[3] J. C. Fuggle, M. Campagna, Z. Zołnierek, R. Lässer, and A. Platau, Phys. Rev. Lett. 45, 1597 (1980).

[4] G. K. Wertheim, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland,

Amsterdam, 1981), p. 67.

[5] S.-J. Oh and S. Doniach, Phys. Rev. B 26, 2085 (1982).

[6] A. Kotani and Y. Toyozawa, Jpn. J. Phys. 35, 1073 (1973); 37, 912 (1974).

[7] K. Schönhammer and O. Gunnarsson, Solid State Commun. 23, 691 (1977).

[8] F. K. Hillebrecht and J. C. Fuggle, Phys. Rev. B 25, 3550 (1982).

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

[10] See, also, for Ce compounds, R. Lässer, J. C. Fuggle, M. Beyss, M. Campagna, F. Steglich, and F. Hulliger, Physica (Utrecht) 102B, 360 (1980).

[11] R. A. Miedema, J. Less-Common. Met. 46, 167 (1976).

[12] O. L. T. de Menezes, A. Troper, P. Lederer, and A. A. Gomes, Phys. Rev. B 17, 1997 (1978).

[13] G. K. Wertheim and C. Crecelius, Phys. Rev. Lett. 40, 813 (1978).

[14] K. A. Gschneidner Jr., T. Takeshita, Y. Chung, and O. D. McMasters, J. Phys. F 12, L1 (1982).

[15] A. Palenzona, Atti Accad. Nazl. Lincei Cl. Sci. Fis. Mat. Nat. Rend. 42, 504 (1967).

[16] F. J. Van Steenwijk, H. Th. Le Fever, R. C. Thiel, K. H. J. Buschow, Physica 79B, 604 (1975).

[17] W. Köster and J. Meixner, Z. Metallkd. 56, 695 (1965).

[18] W. Bronger, J. Less-Common Metals 12, 63 (1967); A. Iandelli and A. Palenzona, J. Less-Common Metals 80, 71 (1981).

[19] A. Iandelli and A. Palenzona, J. Less-Common Metals 38, 1 (1974).

[20] I. R. Harris and G. Longworth, J. Less-Common Metals 23, 281 (1971).

[21] E. R. Bauminger, G. M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts,* edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 661.

[22] H. de Graaf, R. C. Thiel, and K. H. J. Buschow, Physica 100B, 81 (1980).

[23] S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, Chem. Phys. Lett. 29, 491 (1974); S. P. Kowalczyk, Ph.D. thesis, University of California, 1976, (unpublished); C. S. Fadley, in *Electron Spectroscopy,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1978), Vol. II, p. 2.

[24] C. Crecelius, G. K. Wertheim, and D. N. E. Buchanan, Phys. Rev. B 18, 6519 (1978).

[25] J. H. Herbst, J. M. Burkstrand, and J. W. Wilkins, Phys. Rev. B 22, 531 (1980).

[26] B. Johansson, Phys. Rev. B 20, 1315 (1979).

[27] B. Johansson, N. Mårtensson, Phys. Rev. B 24, 4484 (1981).

[28] J. H. Herbst and J. W. Wilkins, Phys. Rev. Lett. 43, 1760 (1979).

[29] B. Johansson, Phys. Rev. B 19, 6615 (1979).

[30] V. Murgai, L. C. Gupta, R. D. Parks, N. Mårtensson, and B. Reihl, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 299.

[31] N. Mårtensson, B. Reihl, W. D. Schneider, V. Murgai, L. C. Gupta, and R. D. Parks, Phys. Rev. B 25, 1446 (1982).

[32] G. Kaindl, B. Reihl, D. E. Eastman, R. A. Pollak, N. Mårtensson, B. Barbara, T. Penney, and T. S. Plaskett, Solid State Commun. 41, 157 (1982); G. Kaindl, C. Laubschat, B. Reihl, R. A. Pollak, N. Mårtensson, F. Holtzberg, and D. E. Eastman, Phys. Rev. B 26, 1713 (1982).

[32] W. Gudat, M. Campagna, R. Rosei, J. H. Weaver, W. Eberhardt, F. Hulliger, and F. Kaldis, J. Appl. Phys. 52, 2123 (1981).

[34] G. K. Wertheim, J. H. Wernick, and G. Crecelius, Phys. Rev. B 18, 875 (1978).

[35] The use of Eq. (1) is only allowed for a homogeneous medium of scatterers. If the scattering length (electron mean free path) is of the order of the nearest-neighbor distance this is certainly not the case. We note that if we assume equidistant discrete scattering centers x_i, the rate of change in the photoelectron current I in the material with traversed length x is given by $dI=-\beta I\delta(x-x_i)dx$, where β denotes the scattering probability. Therefore, $I(x)=\exp(-\beta x_i)$ for $x\in|x_i,x_{i+1}|$. In order to compare this function with the continuous one, $I_c(x)=\exp(-\beta x)$, $x\in R$, we consider the expression

$$\frac{\int_{x_i}^{x_i+1} I\,dx}{\int_{x_i}^{x_i+1} I_c dx}=\frac{\beta\Delta\exp(-\beta x_i)}{\exp(-\beta x_i)-\exp(-\beta x_i+\Delta)}$$

$$=\beta\Delta/[1-\exp(-\beta\Delta)]$$

$$=\text{const}\;,$$

with $\Delta=x-x_i$. The surface (I_S) and bulk (I_B) contributions in the discrete case consequently differ only by a constant factor from the continuous case and vanish for the ratio numbers $V(3d)$ and $V(4d)$.

[36] D. R. Penn, J. Electron. Spectrosc. Relat. Phenom. 9, 29 (1976).

[37] L. I. Johansson, A. Flodström, S. E. Hörnström, B. Johansson, J. Barth, and F. Gerken, Solid State Commun. 41, 427 (1982).

[38] W. D. Schneider, C. Laubschat, G. Kaindl, B. Reihl, and N. Mårtensson, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 277.