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Binding energies and work-function changes in $Eu_xLa_{1-x}Al_2$ compounds studied by x-ray photoelectron spectroscopy

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The intermetallic compound $Eu_xLa_{1-x}Al_2$ has been studied by x-ray photoelectron spectroscopy with Al $K\alpha$ radiation at concentrations $x = 0$, 0.03, 0.1, and 1. The dependence of the Eu-$4f$ line shape on the partial density of states at the Fermi energy is discussed. The Eu-$4f$ excitation energy in the compounds was found to be $\Delta_- = 1.0 \pm 0.1$ eV independent of the Eu concentration. This is 0.9 eV smaller than the value reported for metallic Eu. The energy shift is mainly due to Fermi-energy changes as confirmed by work-function measurements of the samples. The resultant shift is discussed in terms of charge transfer together with existing Mössbauer-isomer-shift data.

I. INTRODUCTION

The physical and magnetic properties of dilute rare-earth alloys are usually explained in terms of a model in which the well-localized $4f$ electrons occupy a very narrow level which lies well below the Fermi surface. It is expected that only the valence $5d$ and $6s$-p electrons will interact appreciably with the host-metal conduction electrons. Exceptions are "intermediate-valence" alloys involving the ions Ce, Yb, or Eu. The isoelectronic Gd^{3+} and Eu^{2+} show quite different effects on the depression of the superconducting transition temperature in La,[1] or $LaAl_2$,[2] the spin-flip relaxation rate in ESR experiments,[3] and the crystal-field splitting.[4] In order to cast some light on the behavior of the localized $4f$ state with alloying, we here report an x-ray photoelectron spectroscopy (XPS) study of intermetallic compounds $Eu_xLa_{1-x}Al_2$ in the range from $x = 0$ to 1. This is of interest also in connection with recent XPS experiments of Wertheim *et al.*[5] on other intermetallic compounds. They found intermediate-valence behavior[6] in $YbAu_2$ and discussed their data in terms of Fermi-energy changes and charge transfer between the constituents of the alloy. Both Eu and Yb do not obey the general trend of decreasing lattice constants with increasing atomic number in the rare-earth elements.[7] In the compounds studied here, the lattice constant changes only slightly over the concentration range from $a = 8.145$ Å for $LaAl_2$ to $a = 8.125$ Å for $EuAl_2$. Volume effects can safely be neglected in these compounds enabling one to focus attention on the electronic properties of the system. In Eu metal the localized $4f$ level was found to be 1.9 eV below the Fermi energy[8,9] in agreement with recent calculations of Herbst *et al.*[10] They call this energy the $4f$ excitation energy Δ_-. The closeness of this localized state to the Fermi level and its high photoionization cross section for the XPS excitation energies make Eu compounds attractive to study. The consequences of alloying can be followed in alloys with as little as 3 at.% of Eu. Furthermore in going from $EuAl_2$ to $LaAl_2$ these compounds offer the opportunity to study the influence of increasing electron concentration on the localized state. This because La introduces an additional valence electron to the system. Measurements of this effect can be correlated with existing Mössbauer-isomer-shift data on these same compounds.[11]

II. EXPERIMENTAL DETAILS

The samples of $Eu_xLa_{1-x}Al_2$ with $x = 0$, 0.03, 0.1, and 1 were prepared by arc melting in argon atmosphere. To ensure homogeneity the ingots were remelted several times. An x-ray structure analysis of all samples indicated that only the single Laves phase was present. The lattice constants agreed with the published values. The Eu concentration was determined independently by a measurement of the saturation magnetic moment at low temperatures, assuming $7.94\mu_B$/ion.

The XPS measurements have been performed in a VG ESCA 3 electron spectrometer with an Al $K\alpha$ x-ray source. The standard sample holder of the instrument was substituted by a metal rod holding the sample by means of a conducting Ag adhesive. In this way any contribution of the sample holder to the spectrum was eliminated.

The base pressure in the spectrometer chamber was about 4×10^{-10} Torr. Even at these pressures there was a O-$1s$ signal growing during the measurements. The thickness of this surface oxygen layer has been calculated by the methods of Penn,[12] to grow to at most 0.1 monolayers in thirty minutes. The samples were therefore cleaned *in situ* in the sample preparation chamber (1×10^{-9} Torr) by abrasing the sample surface with a diamond file every 15 minutes.

The resolution function of the spectrometer (slits, 2 mm; analyzer voltage of 20 eV) has been determined by a least-square analysis of the Au $4f_{7/2,5/2}$ doublet. The model function used was a convolution of a Doniach-Šunjić [13] (DS) line shape with two Gaussian-broadened Lorentzians. The latter two originate from the $K\alpha_1$ and $K\alpha_2$ x rays. We obtained a resolution function of 1.0 eV full width at half maximum (FWHM) mainly due to the inherent $K\alpha_{1,2}$ x-ray linewidth. The position of the Fermi level of the samples has been located by reference to the Au-$4f_{7/2}$ (84.0 eV) line of vacuum-evaporated Au on the same surface. The accuracy of this method was found to be ±0.06 eV.

In order to determine the work functions of the samples the onset of the secondary emitted electrons on the low kinetic energy side of the photoemission spectrum was recorded.[14] In this way contact potential differences of the samples relative to the spectrometer are measured. By choosing Al as a reference[15] ($\phi = 4.3$ eV) we deduced to an accuracy of ±0.05 eV the work functions summarized in Table I. With this calibration we obtained for Au, 5.1 eV and for Eu, 2.7 eV which is in very good agreement with data of Eastman.[16]

As Evans [17] pointed out, this method of determination of work functions is not a trivial operation with a VG ESCA 3 instrument. We will therefore briefly sketch the experimental setup. In the normal scanning mode the kinetic energy of the photoemitted electrons is varied by changing the retarding potential of the sample; the electrical midpoint of the hemispherical analyzer is grounded. Therefore at low kinetic energies the electrons originating from the sample are masked by the secondary electrons originating from the Faraday cup surrounding the sample area. In order to detect the electrons from the sample, we (i) have grounded the Faraday cup and disconnected it from the sample holder, (ii) applied a negative bias voltage (40 V) to the sample in order to accelerate electrons emitted from the sample, and (iii) applied the scanned retarding potential to the electrical midpoint of the analyzer hemispheres.

III. RESULTS AND DISCUSSION

In Fig. 1 the XPS spectra of the $4f$ level, the valence band, as well as the $5p$-core-level region of Eu, EuAl$_2$, Eu$_{0.10}$La$_{0.90}$Al$_2$, Eu$_{0.03}$La$_{0.97}$Al$_2$, and LaAl$_2$ are shown. Furthermore, spectra from the Eu-$4d$ core-level region in the compounds were recorded. Measurements on metallic Eu have been performed in order to check the reliability of our analysis. Table I summarizes the energies of the relevant features of the spectra. The pure host compound LaAl$_2$ shows, apart from the structure around 7 eV, which is due to

TABLE I. Electron binding energies and work functions in Eu$_x$La$_{1-x}$Al$_2$ compounds and their constituents.

Material	Work function (eV)	Level	Binding energy (eV)	Shift (eV)	Work-function correction (eV)	Resulting shift (eV)
Eu	2.7 ±0.05	Eu $4f$	1.8 ±0.1	. . .	. . .	. . .
EuAl$_2$	3.3 ±0.05	Eu $4f$	1.0 ±0.1	−0.8	+0.6	−0.2
Eu$_{0.10}$La$_{0.90}$Al$_2$	4.1 ±0.05	Eu $4f$	1.0 ±0.1	−0.8	+1.4	+0.6
Eu$_{0.03}$La$_{0.97}$Al$_2$	4.1 ±0.05	Eu $4f$	1.0 ±0.1	−0.8	+1.4	+0.6
Al	4.3[a]	Al $2p_{3/2}$	72.5 ±0.2[b]	. . .	. . .	. . .
EuAl$_2$	3.3 ±0.05	Al $2p_{3/2}$	72.8 ±0.2	+0.3	−1.0	−0.7
LaAl$_2$	4.2 ±0.05	Al $2p_{3/2}$	72.6 ±0.2	+0.1	−0.1	±0.0
La	3.5[a]	La $5p_{3/2}$	16.8 ±0.3[b]	. . .	. . .	. . .
LaAl$_2$	4.2 ±0.05	La $5p_{3/2}$	17.1 ±0.3	+0.3	−0.7	−0.4
Eu	2.7 ±0.05	Eu $5p_{3/2}$	18.2 ±0.1	. . .	. . .	. . .
EuAl$_2$	3.3 ±0.05	Eu $5p_{3/2}$	17.9 ±0.3	−0.3	+0.6	+0.3
Eu	2.7 ±0.05	Eu $4d(^9D)$	129.2 ±0.2[b,c]	. . .	. . .	. . .
EuAl$_2$	3.3 ±0.05	Eu $4d(^9D)$	129.8 ±0.5[c]	+0.6	+0.6	+1.2
Eu$_{0.10}$La$_{0.90}$Al$_2$	4.1 ±0.05	Eu $4d(^9D)$	129.9 ±0.5[c]	+0.7	+1.4	+2.1

[a] Reference 15.

[b] Reference 37.

[c] Mean energy only.

$K\alpha_{3,4}$ satellites of the La-$5p$ spin-orbit doublet, a relative broad and featureless valence band which extends to about 12 eV below E_F. It appears like a free-electron density of states, in agreement with Ref. 8, where data on a couple of rare-earth dialuminides was discussed. We focus our attention on the $4f$ levels in the immediate neighborhood of the Fermi energy. Viewing from top to bottom of Fig. 1, the intensity of the Eu $4f$ state decreases relative to the Eu-$5p$ and La-$5p$ peaks with decreasing Eu concentration. Furthermore there is a shift in the Eu-$4f$ binding energy of about 0.8 eV (see also Table I) in going from the pure metal to the compound $EuAl_2$ or the ternary systems.

Comparing the $5p$ emission in $EuAl_2$ and $LaAl_2$ the favorable cross-section ratio $\sigma(\text{Eu } 4f)/\sigma(\text{Al } 3s, 3p; \text{La } 5d\ 6s)$ is apparent. Therefore the $4f$ photoemission line shape was investigated for Eu metal as well as for the compounds. (The $K\alpha_{3,4}$ satellite contribution has been subtracted in a first step of the analysis.) The results are shown in Fig. 2. The data of the compounds contain a superposition of the $4f$ and the valence-band emission. They could be analyzed quantitatively because the valence-band contribution is relatively featureless. It has been subtracted in the two ternary compounds under the assumption that it is like the one of $LaAl_2$. The analysis was carried out

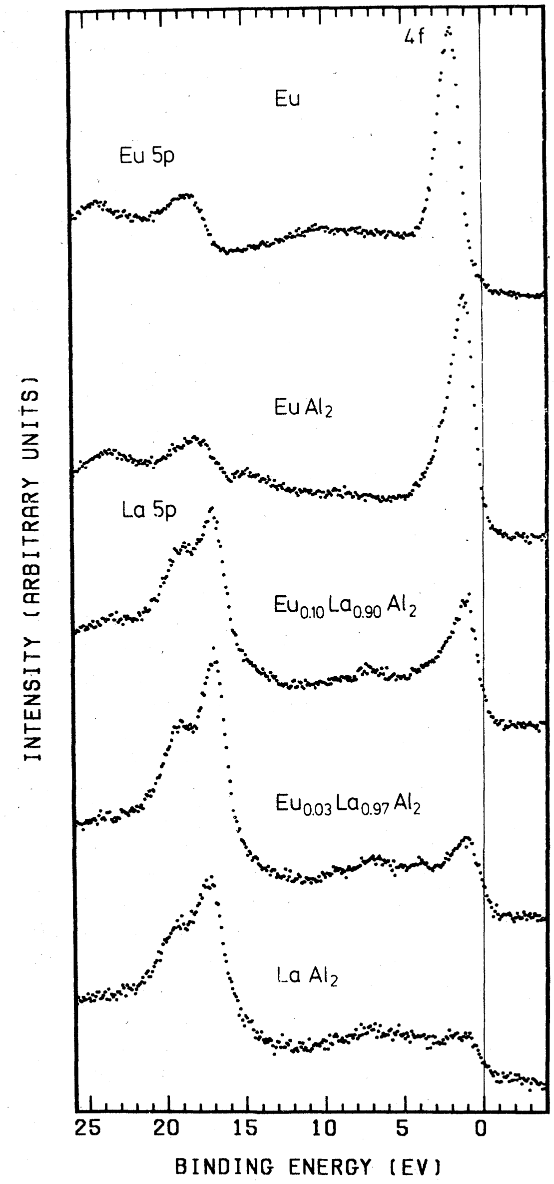

FIG. 1. Experimental XPS spectra of the $4f$ and the $5p$ core-level region of Eu and the intermetallic compounds $Eu_xLa_{1-x}Al_2$ excited with Al $K\alpha$ radiation.

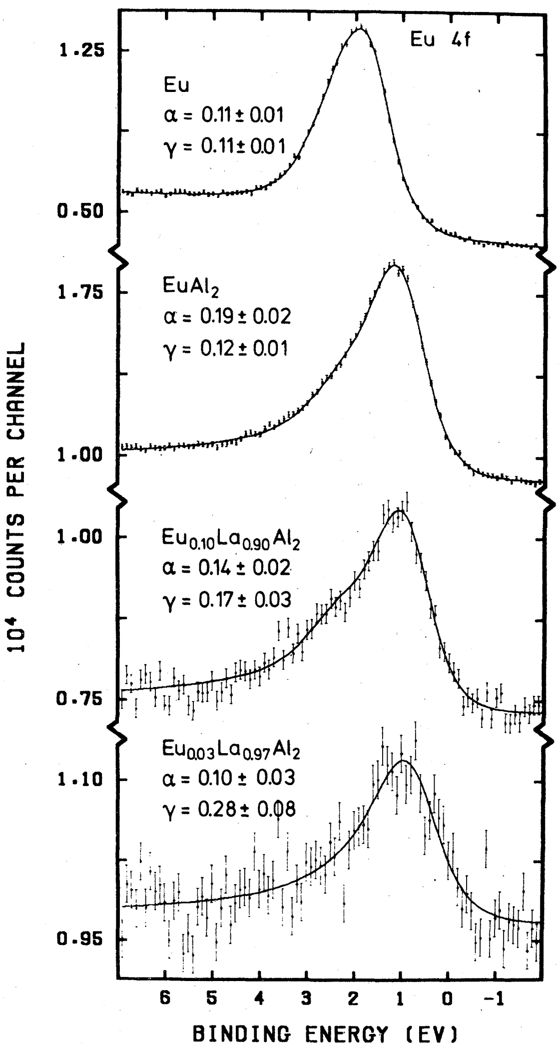

FIG. 2. Eu-$4f$ final state in the metal and in the intermetallic compounds. The full curve represents the result of a Doniach-Šunjić line-shape analyis.

by assuming a DS line shape convoluted with the spectrometer resolution function. Data analysis with the DS line shape is only strictly applicable to simple metals with broad conduction bands.[18] We therefore expect the results to be only an approximation to the true photoemission spectrum. The intensities[19] and energy separations[20] of the individual J levels of the $^7F_0$ final-state multiplet of Eu^{2+} have been used in the analysis. The best fit to the data could be achieved by taking into account an integral contribution of a background due to inelastic scattering[21] and a weak feature of the high binding-energy side in the spectra of Eu and Eu compounds. The latter is most likely ascribed to a small oxygen contamination.

We note the following observation for the singularity index α, which describes the phase shift for scattering of conduction electrons from the hole potential in the photoemission process: There is a substantial increase in α in going from the Eu metal to the compound $EuAl_2$ followed by a decrease in the ternary diluted compounds (see Fig. 2). A comparison with earlier data[22] on metallic Eu [by using the asymmetry-parameter-to-singularity-index conversion table of Ref. (13)] yields good agreement with our data analysis.

It is well known[23,24] that α depends on the local density of states of the electrons at the Fermi level. In order to get a more quantitative picture of the relationship between the singularity index α and the local screening charge we calculated on the basis of free-electron phase shift s and p screening charges at different constant d screening charges for various values of α. The analysis was carried out by using the Friedel sum rule with

$$Z = \sum_l q_l = 1 \; ;$$

and α was expressed in terms of partial screening charges,

$$\alpha = \sum q_l^2/2(2l+1),$$

where l denotes the orbital angular momenta $(l = 0, 1, 2)$.[23] The result is shown in Fig 3, where the minima of the curves are located between the minimum values of α for s, p, and d screening charges with $\alpha_{\min} = \frac{1}{18}$ and for s and p screening charges with $\alpha_{\min} = \frac{1}{8}$ One can try to get some insight into the screening process by locating the measured value of α for Al [$\alpha = 0.12$ (from Ref. 23)] in Fig. 3. If one makes the reasonable assumption that only s and p screening charges are important for the simple sp metal Al we localize the corresponding screening charges of about 75% p screening and 25% s screening in the minimum of the $q_2 = 0$ curve. Consequently any increase in s or p screening charge and no considerable contribution from d screening would yield an increase in α. By forming the intermetallic compound $EuAl_2$ we measure an increase in α for the Al-2s line as well as for the Eu-4f line, indicating an increase in s or p screening charge. In the ternary compounds where Eu is diluted in a $LaAl_2$ matrix our line-shape analysis yields decreasing values for α. On the basis of a nonrelativistic APW band-structure calculation of Switendick [25] who calculated partial density of states for the Laves-phase compound $LaAl_2$ one expects a change in the local density of states at the Eu sites due to the increased d-character of the conduction electrons contributed by La. In the picture of free-electron screening charges (see Fig. 3) an additional d screening charge would predict decreasing asymmetry. This is in agreement with our measurements. One could attempt to go one step further and compare the measured value for α with the theoretical density of states of Switendick. His partial density of states calculation yields mainly p- and d-electron contribution at the Fermi level. (Apart from an f-electron contribution which is doubtful in the case of $LaAl_2$.) For $\alpha \cong 0.1$ and no s screening one places the resulting p and d screening charge in the upper left part of Fig. 3, making the p screening charge about 3 times the d screening charge. This ratio is a factor of 1.5 higher than the theoretical ratio from Switendick's calculation. We must keep in mind, however, that the considerations about partial screening charges are strictly valid for free electrons only.

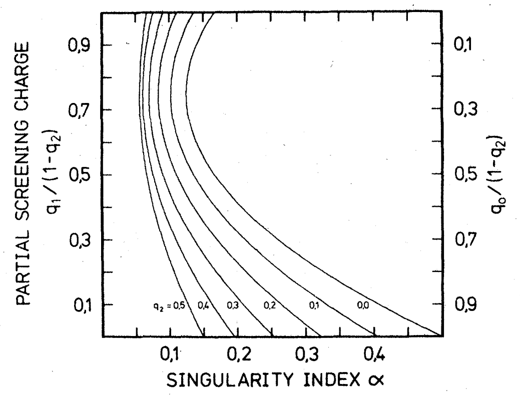

FIG. 3. Partial screening charges as a function of singularity index in a three-screening-charge analysis using the Friedel sum rule with $Z = 1$.

Our line-shape analysis for Eu metal yields a lifetime width of 0.11 ±0.02 eV. This is in agreement with earlier measurements on metallic Eu and Sm, where the lifetime widths were estimated from the data. The investigation of the rare-earth borides[26,27] has shown that the lifetime width (i) is proportional to the number of 4f holes present after photoemission, (ii) decreases sharply with decreasing 4f binding energy, and (iii) increases with the number of anion neighbors. The magnitude of the linewidth is due to an Auger recombination effect. We observe no difference in the Eu-$4f$ lifetime width between Eu metal and $EuAl_2$. Because in both cases the emission from the $^7F_0$ final state with 9 holes is observed there is no effect from item (i). From the change in $4f$ binding energy of about 1 eV towards the Fermi level in going from Eu metal to $EuAl_2$ one would expect a decrease in lifetime width, regarding item (ii). On the other hand there is a change in crystal structure from bcc to the cubic Laves phase which affects the coordination of the Eu ions. In Eu metal the coordination is 8 and the nearest-neighbor distance $a\sqrt{3}/2=3.96$ Å (with $a=4.58$ Å). In $EuAl_2$ the coordination to the next Eu ions is four other equidistant Eu atoms at a distance $a\sqrt{3}/4=3.5$ Å (with $a=8.12$ Å) and twelve Al atoms at a somewhat smaller distance $a\sqrt{11}/8=3.4$ Å. The coordination is then effectively 16.[28] So one would expect an increase in lifetime width from the increase in the number of next-neighbor atoms. Effects (ii) and (iii) seem to cancel each other in $EuAl_2$.

In the dilute compounds there is an increase in lifetime width of the Eu $4f$ state compared to $EuAl_2$. Here we expect again no contribution from effect (i) because the number of holes is not altered, (ii) because there is no shift in binding energy, and (iii) because the number of nearest neighbors is not changed. ($LaAl_2$ has the same crystal structure.) But there is a change in the density of states due to the La neighbors thereby increasing the $5d$-$4f$ interatomic Auger recombination rate. This would predict an increase in lifetime width which is in agreement with our analysis.

Now we discuss the difference between the Eu-$4f$-state binding energy in the metal and in the intermetallic compounds. As Watson and Perlman[29] pointed out, in interpreting binding-energy shifts, one has to refer to a common zero of binding energy, which is the vacuum zero of the sample ("absolute binding energy"). The kinetic energies of the electrons are always measured with respect to the work function of the spectrometer[30] rather than that of the sample. In order to compare binding energies one has to consider therefore work function changes (representing Fermi energy changes) of the constituents upon alloy formation.

Here we should include a comment regarding the work function of alloys $EuAl_2$ and $LaAl_2$. The work function of binary compounds is often assumed to be the weighted mean of the constituents.[5,29] This method would lead to a value of 3.8 eV for $EuAl_2$ whereas we measured 3.3 eV, and in the case of $LaAl_2$ to 4.0 eV where we measured 4.2 eV (see Table I). In $EuAl_2$ it is the low work function component which is favored and in $LaAl_2$ it is the high work function component which dominates. For $EuAl_2$ there is a substantial discrepancy (0.5 eV) between the measured value and the weighted mean. In a recent review article, Hölzl and Schulte[31] show similar rather peculiar examples of the composition dependence of the work function in the alloys Mo-W and Ag-Pd.

We took the values for the work functions of the compounds measured in this work and applied this work function correction to the measured binding-energy shifts displayed in Table I.

The work function correction leads in most cases to a reversed direction of the shifts. The resultant shift of the core levels can be interpreted as a charge transfer from Eu to Al and from La to Al which is in agreement with the electronegativity scale of Pauling[32] in which Eu and La are assigned a value of 1.1 and Al a value of 1.5. The localized Eu $4f$ levels do not follow this simple picture as discussed below. The main effect in the binding-energy difference (relative to E_F) between Eu metal and $EuAl_2$ is evidently due to the different work functions in the element and relative to that in the compound. This result is illustrated in Fig. 4, shown as a schematic level diagram of the systems studied including the corresponding work functions. On the left-hand side of this diagram we have plotted characteristic levels of Eu, $EuAl_2$, and Al. Neglecting for the moment volume changes and charge transfer one would expect the Eu $4f$ level to be constant in absolute binding energy (relative to vacuum zero). This would lead to a smaller excitation energy of the Eu $4f$ state in the compound compared to the element. And indeed, in spite of a volume change of about 10% due to the lattice contraction in going from Eu metal with bcc structure to $EuAl_2$ with the cubic $MgCu_2$ Laves-phase structure, we find the Eu $4f$ level in the compound nearly at the same absolute binding energy within the error of the experiment. This result is in excellent agreement with an investigation of Wertheim *et al.*[18] who showed with Ca-substituted SmS that the $4f$ binding energies do not depend on

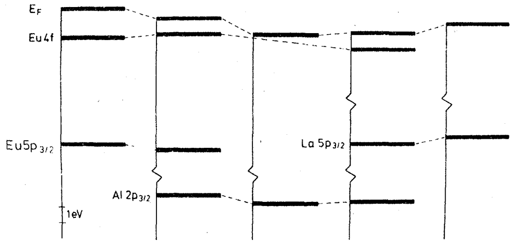

FIG. 4. Schematic representation of the electronic levels in the intermetallic compounds $Eu_xLa_{1-x}Al_2$ and their constituents on an absolute binding-energy scale. The width of the levels include the estimated experimental error.

lattice constant. It is noticeable from Table I and Fig. 4 that the $4f$ level of Eu moves in opposite direction compared to the $5p$ and $4d$ level when $EuAl_2$ is formed. The Eu-$5p$ and -$4d$ shifts to higher absolute binding energy indicate charge transfer from Eu to Al, which is consistent with the Al-$2p$ core-level shift in the compound. We therefore interpret the Eu-$4f$ shift to smaller absolute binding energies in $EuAl_2$ as a final-state effect due to increased screening of the hole state by conduction electrons.[18] On the right-hand side of Fig. 4 we have chosen to summarize the data for $LaAl_2$ and the ternary compounds with Eu concentrations of 3 at.% and 10 at.% in a single row, this because the Fermi energy changes very little over this concentration range (see Table I).

Since the Fermi energy of the ternary compounds is lower one would expect, from the arguments given above, that the Eu $4f$ state would be even closer to the Fermi surface than in $EuAl_2$, this leading to a situation where an intermediate-valence phenomenon might occur. Instead a shift to higher absolute binding energy is evident. One might argue that the extra electron which La^{3+} contributes is responsible for this shift. The change in the conduction-band occupancy may give rise to a repulsive Coulomb interaction which pushes the Eu $4f$ state to higher absolute binding energy.

Considering the complete diagram of Fig. 4, we conclude that the difference in Eu-$4f$ excitation energy between Eu and $EuAl_2$ is mainly due to Fermi energy changes as a consequence of alloying. As was demonstrated by Wertheim *et al.*[5] in $YbAu_2$, in principle the $4f$ level might even be shifted above the Fermi energy by choosing the appropriate element with a greater electronegativity and therefore a higher work function. Another example of an intermediate-valence state which fits in with the general model is $EuRh_2$.[33] The electronegativity of Rh is greater than that of Al, leading to greater charge flow from Eu to Rh. [The investigation was done on the Eu $4d$ levels, where the two final-state configurations became obvious. We could not detect a valency other than Eu^{2+} in our spectra consistent with Mössbauer measurements (Ref. 34).] However in the ternary compounds with dilute Eu concentrations studied here the Eu $4f$ level remained constant in excitation energy independent of the Eu concentration. Therefore we are lead to say that Fermi energy charges alone do not suffice to predict an intermediate-valence behavior.

Watson and Perlman[29] compare binding-energy shifts measured by XPS with those from Mössbauer isomer shifts and it is interesting to apply their arguments to the system studied here. Taking values from the literature[35] one finds the isomer shift decreases from Eu metal to Eu in $EuAl_2$ indicating a lower electron concentration at the Eu nucleus in $EuAl_2$. One is tempted to say that there is s-charge flow from Eu to Al in the compound in agreement with the direction of the absolute binding-energy shifts (of the Al $2p$ and Eu $5p$ level) measured in this work.

For the ternary systems studied here, Mössbauer measurements exist as well. Nowik *et al.*[11] found that within the experimental error the isomer shift was independent of the Eu concentration. They interpreted this result by assuming that the isomer shift in these compounds depends only on the electrons which Eu contributes to the conduction band and not to the local atomic environment of the Eu atom. As is stated in Ref. 35, this is a rather peculiar behavior since La contributes a full additional electron in going from $Eu^{2+}Al_2$ to $La^{3+}Al_2$. Taking the value of α measured by XPS (see Fig. 2) into consideration (which can be interpreted as an increase in d-electron density as a function of La concentration) one might argue that an increase in d-electron density has a much weaker influence on the isomer shift and therefore is more difficult to observe. In this context it is interesting to note that recent isomer shift measurements[34] on the samples studied here indeed show an increase, relative to the value for $EuAl_2$, of $(0.5 \pm 0.04)\%$ per at.% La concentration, i.e., a higher electron density at the Eu nucleus. This can be understood as a consequence of a hybridization of the $5d6s$ bands upon alloying.[36]

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