Final-state effects in divalent Eu pnictides

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Abstract. From Mössbauer effect, lattice constant and susceptibility measurements we show that Eu is nearly divalent in Eu(Cu, Ag, Au)(P, As, Sb). However, the L_{III} x-ray absorption spectra consist of a pronounced double structure, suggesting a non-integral mean Eu valence. The high-energy structure in the L_{III}-edge spectra is interpreted as a final-state (shake-up) effect. This finding strongly supports the existence of final-state effects in the L_{III} x-ray absorption spectra of divalent Eu compounds as previously reported by Sampathkumaran and co-workers in $EuPd_2P_2$.

1. Introduction

L_{III} x-ray absorption spectroscopy (XAS) on rare earth (RE) atoms has often been used to determine the RE valence [1]. At the absorption edge a strong 'white line' (WL) is found due to the transition of the $2p_{3/2}$ electron into the relatively narrow 5d band with its high density of states. Due to the different screening, the position of the absorption edge for different valences of an RE ion is shifted by 7–10 eV depending on the RE. If a double-peaked structure at the absorption edge is observed, as in (statically or dynamically) mixed valent systems, the (mean) valence is obtained from the ratio of the intensities of the two white lines, corresponding to the $4f^n$ and $4f^{n+1}$ states.

The above-sketched scenario is called the single-particle picture [2]. Here, it is assumed that the 4f occupation number does not change during the absorption process (no final-state effect). However, it is well known that 'shake-down' effects play an important role in the compounds of light REs [3]. Due to the attractive Coulomb potential of the core hole the 4f level is lowered. Therefore the 4f state can be occupied by a conduction electron, thereby increasing the 4f number. From photoelectron spectroscopy (XPS) it is well known that the reverse ('shake-up') effect also occurs [4]: a 4f electron is ejected into the conduction band, thereby decreasing the number of 4f electrons.

The question of whether such shake-up effects also occur in nearly divalent Eu compounds remains a matter of controversy. A typical case is that of $EuPd_2P_2$. The L_{III} spectrum shows a double-peaked structure; the intensity of the structure, which is 7.7 eV higher in energy, amounts to 15% [5], at first sight indicating intermediate valency of the Eu ions. However, susceptibility, Mössbauer effect [6] and valence-band photoemission [7] show the divalent character of Eu in this compound. Therefore, Sampathkumaran and co-workers [5] conclude that the high-energy peak in the L_{III} absorption spectrum (and in the 3d core-level XPS [7]) is due to a shake-up effect. This conclusion is rejected by Röhler [8].

In his interpretation, susceptibility and Mössbauer effect measurements are still compatible with intermediate-valence Eu in $EuPd_2P_2$.

In this paper we report on L_{III} XAS, Mössbauer effect and lattice constant measurements of the nine compounds Eu(Cu, Ag, Au)(P, As, Sb) (1–1–1 compounds). In our discussion we also refer to the susceptibility data of Tomuschat and Schuster [9, 10]. All compounds crystallize in the hexagonal Ni_2In structure [9]. Previous studies of the isostructural compounds EuPtP [11, 12], EuPdP, EuNiP [13, 14] and EuPdAs [15] have shown that in these compounds Eu is mixed valence and shows one or two phase transitions with a valence jump of about $\frac{1}{6}$. Here, we are interested in the Eu valence of the isostructural compounds with the noble metals Cu, Ag, Au instead of Ni, Pd, Pt. Our results lead us to the conclusion that final-state effects are important in the interpretation of the XAS spectra of these compounds.

2. Results

2.1. Sample preparation and lattice constants

The samples were prepared as described previously [9]. They were checked for impurity phases by x-ray powder diffraction. In all samples the content of impurity phases was smaller than $\sim 7\%$. Particularly in the samples used for L_{III} XAS and Mössbauer effect, we could not detect any impurity phase within an accuracy of about 3% (except EuAgAs with about 5% impurity phase).

Table 1. Magnetic data (after [9, 10]), cell volumes and L_{III} valences of the 1–1–1 compounds.

	p_{eff} [μ_B]	Θ [K]	T_{mag} [K]	Type	V[Å^3]	$\nu(L_{III})$
EuCuP	7.64	41	37	Ferro	120.7	2.13
EuAgP	7.52	20	18	Ferro	134.4	2.16
EuAuP	7.68	22	17	Ferro	133.0	2.18
EuCuAs	7.67	28	18	Meta	129.7	2.15
EuAgAs	7.45	19	11	Meta	143.2	2.22[a]
EuAuAs	7.57	11	8	Ferro	142.0	—
EuCuSb	7.72	7	12	AF	150.6	—
EuAgSb	7.62	2	8	AF	162.2	—
EuAuSb	7.60	6	10	AF	160.3	2.15[b]

[a] About 5% impurity phase.
[b] From laboratory spectrometer.

The lattice constants of our samples were determined by x-ray powder diffraction and the resulting volumes are listed in table 1. They agree well with those reported previously [9]. In figure 1 they are shown together with those of the isostructural alkaline earth compounds [16–18] against their respective ionic radii. For the Eu compounds we took the divalent radius $r^{2+} = 1.12$ Å [19]. As far as the alkaline earth compounds exist, there is a striking linear relationship between the unit cell volumes and the divalent ionic radii in each series, in which Eu fits very well. It is worth mentioning that in several series

A(Cu, Ag, Au)(P, As, Sb) the compounds with the relatively large A = Sr, Ba and Eu ions exist, but those with the smaller Ca ion do not exist (at least not in the Ni_2In structure). The reverse case does not occur (see figure 1).
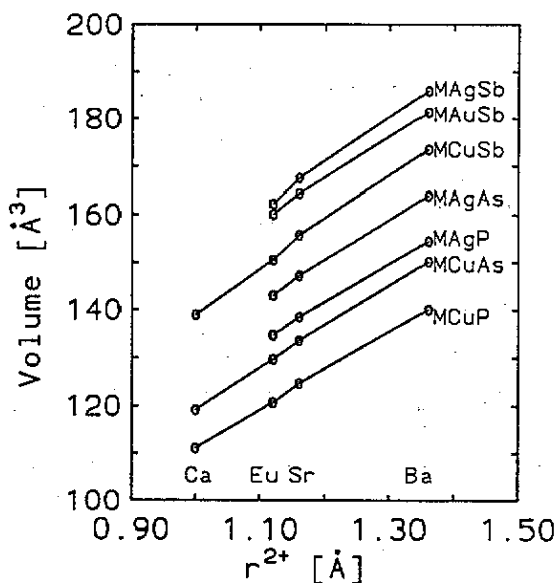

Figure 1. Unit cell volumes of the alkaline earth and Eu 1–1–1 compounds in Ni_2In structure against divalent ionic radii.

We have also investigated the temperature dependence of the lattice constants of EuAuAs between 4.2 and 300 K. The thermal expansion is of the order of $5 \times 10^{-5}\,K^{-1}$ at 300 K and there are no anomalies down to 4.2 K.

2.2. Mössbauer spectroscopy

For Mössbauer measurements a 100 mCi $^{151}SmF_3$ source at room temperature was used. Two samples, EuCuP and EuAuP, were investigated at 300 K. The spectra are shown in figure 2. Both spectra consist of a single line at $-10.83(3)\,mm\,s^{-1}$ and $-11.56(3)\,mm\,s^{-1}$ for the Cu and Au compound, respectively. These values are clearly in the energy range for divalent Eu (≈ -8 to $-12\,mm\,s^{-1}$) in metallic compounds. Within the resolution of our experiment ($\sim 3\%$), we could not detect any second line in the region of $0\,mm\,s^{-1}$, typical for Eu^{3+}. The line widths of $2.86\,mm\,s^{-1}$ and $2.61\,mm\,s^{-1}$ for the Cu and Au compound respectively are in the usual range for stable-valence Eu compounds. We also recorded Mössbauer spectra at 77 K. The spectra still consist of a single line at the same position ($\pm 0.08\,mm\,s^{-1}$) as at 300 K. Due to thermal expansion we expect a difference of the isomer shifts at 77 K and 300 K of less than $0.1\,mm\,s^{-1}$ ($\partial S/\partial \ln V \approx -9\,mm\,s^{-1}$ [20]). The occurrence of only one Mössbauer line here is quite different from that reported for EuPdAs [15], EuNiP, EuPdP [13, 14] and EuPtP [11]. There we found two Mössbauer lines at $\sim -10\,mm\,s^{-1}$ and $\sim 0\,mm\,s^{-1}$.
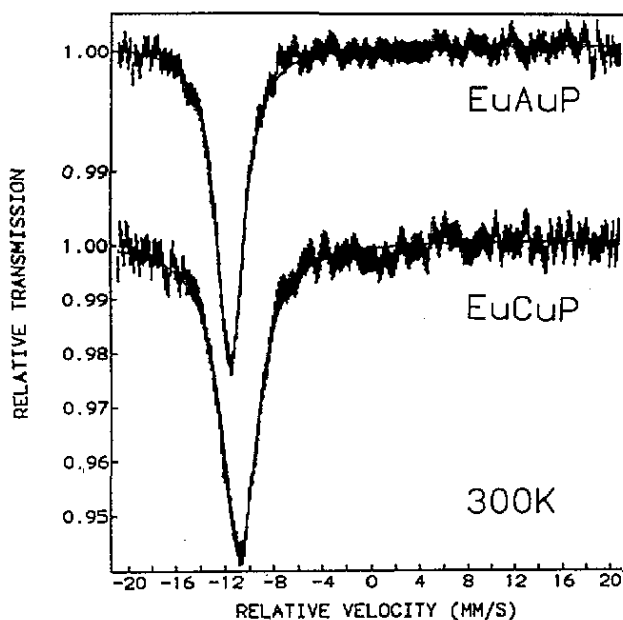
Figure 2. ^{151}Eu Mössbauer absorption spectra of EuCuP and EuAuP at 300 K.

2.3. Susceptibility

The susceptibilities of the compounds were measured by Tomuschat and Schuster [9, 10] with a Faraday balance. Above the magnetic ordering temperature the susceptibilities of all samples follow a Curie–Weiss law. The parameters are given in table 1. The effective moments (p_{eff}) of all samples are in the region 7.4–7.7 μ_B. These values are very close to the value of the effective moment of the free Eu^{2+} ion (7.94μ_B). In the Wohlleben–Sales model they would correspond to an Eu valency of 2.07 [21]. However, effective moments derived from the Curie–Weiss behaviour are not a very exact measure for the valence (see below).

All samples order magnetically above 4.2 K. The compounds with a cell volume less than $\sim 140 \text{\AA}^3$, i.e. all phosphides and also EuAuAs, order ferromagnetically, while the larger antimonides order antiferromagnetically. EuCuAs and EuAgAs show metamagnetism. The ordering temperatures scale more or less with the cell volumes. It is remarkable that for all systems the Curie–Weiss temperature is positive, even for compounds with antiferromagnetic ordering.

2.4. X-ray absorption

L_{III} XAS measurements were performed at the French synchrotron facility LURE, experimental station XAS2, with an Si 113 double monochromator and mirrors to suppress the harmonics below 10^{-5}. The beam energy was 1.85 GeV, the maximum current 325 mA. For EuCuP and EuAuP we used the *same* absorbers as in the Mössbauer measurements, which were performed *after* the XAS measurements.

The room temperature spectra of the phosphides Eu(Cu, Ag, Au)P and of the arsenides Eu(Cu, Ag)As are shown in figure 3. They clearly exhibit a double-peaked structure. The normalization to an absorption step of one was a bit ambiguous, because of the strong
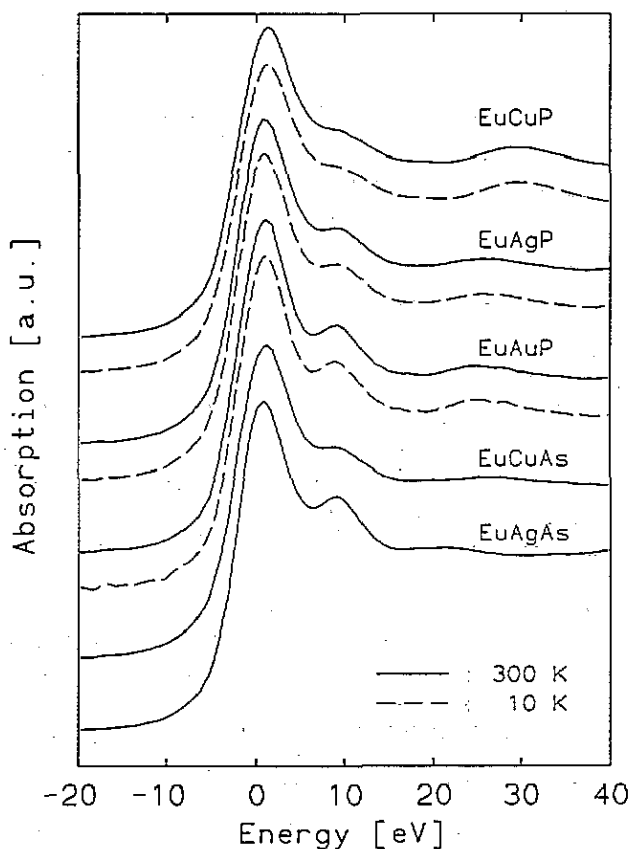
Figure 3. L_{III} x-ray absorption spectra of some of the 1–1–1 compounds at 300 K and 10 K.

XANES structures also visible in figure 3. In a first step we identified the high-energy peak as a WL of Eu^{3+}. To obtain the 'L_{III} valence', we fitted the normalized spectra with an arctan function and a Voigt profile (a Lorentzian convoluted with a Gaussian function) for each structure. The obtained valences at room temperature are given in table 1. They are of the order 2.12...2.22. The uncertainty in the valences is about 0.02...0.03, mainly due to uncertainties in the normalization procedure. For the phosphides the L_{III} valence increases with the atomic number of the transition element. In all cases the energy separation of the two lines is between 8.1 and 8.4 eV.

For the phosphides we have also measured L_{III} spectra at 10 K (broken curves in figure 3). They agree perfectly with the spectra at room temperature. The differences of the valence values are smaller than 0.004 for all compounds.

With our laboratory spectrometer [22] (W tube, Si 113 monochromator), we have also performed temperature-dependent measurements on EuAgP, EuAgAs and EuAuSb between 300 and 10 K [14, 23]. Again, in all cases we find a double-peaked structure at the absorption edge that is independent of temperature.

3. Discussion

The above-described measurements show a clear discrepancy between the Eu valences obtained from different methods. From the lattice constants, susceptibility and Mössbauer effect we have to conclude that Eu is nearly divalent in these compounds. On the other hand, the L_{III} spectra show a double structure indicating a mixed-valence case. Therefore we first discuss the reliability of the different methods indicating the divalency of Eu in the investigated compounds. Then, based on this discussion, we will reinterpret the L_{III} spectra.

3.1. Valence determination from lattice constant, Mössbauer effect and susceptibility measurements

Due to the sizable difference of the ionic radii of Eu^{2+} and Eu^{3+}, the magnitude of the cell volume of an Eu compound compared with those of suitable reference compounds can provide some information on the Eu valence in the compound. Usually, the isostructural trivalent RE compounds are taken as reference systems (see, for example, [24]). In this case a volume anomaly of the Eu compound indicates that Eu is either mixed valence or divalent. A comparison with a series of isostructural divalent alkaline earth compounds is seldom possible. In our study we have this rare case: the trivalent RE(Cu, Ag, Au)(P, As, Sb) compounds do not exist, while there are many of the (divalent) alkaline earth compounds. Therefore we are not concerned with an anomaly with respect to trivalent ions, but with the absence of an anomaly with respect to divalent ions. So we can conclude, almost unambiguously, the divalency of Eu in these compounds.

From Mössbauer isomer shift measurements it is possible to distinguish between inhomogeneously (static) mixed-valence (two separated lines at $\sim 0\,mm\,s^{-1}$ and $\sim -10\,mm\,s^{-1}$) and intermediate-(fluctuating) valence (one line at an intermediate position). The absence of a trivalent Mössbauer line around $0\,mm\,s^{-1}$ clearly excludes an inhomogeneously mixed valent state. It further excludes the existence of larger amounts ($> 3\%$) of Eu^{3+} impurities, e.g. Eu_2O_3. In general, however, it is difficult to distinguish between slightly intermediate valence and divalence from Mössbauer spectroscopy, because the isomer shift of the divalent state is not accurately known. In our case it is a little easier: the isomer shifts of less than $-10.7\,mm\,s^{-1}$ are clearly in the divalent region for metallic compounds that extends between $-8\,mm\,s^{-1}$ and $-12\,mm\,s^{-1}$ in metallic systems. Furthermore, the divalence of Eu in our compounds is strongly supported by the fact that the isomer shifts are more negative than the isomer shifts of the divalent lines of the isostructural inhomogeneously mixed valence compounds EuPdAs [15], EuNiP, EuPdP [13, 14] and EuPtP [11] ($> -10.7\,mm\,s^{-1}$).

The temperature dependence of the isomer shift can give information about the thermal admixture of the trivalent $4f^6$ state to the divalent $4f^7$ ground state. If there is an admixture, the isomer shift will tend to more positive values with increasing temperature due to the increasing thermal population of the $4f^6$ state. Indeed, this has been observed in EuO under high pressures above $19\,GPa$, where the $4f^7$ state becomes unstable [25]. However, in our compounds we find no temperature dependence of the isomer shift between 77 and 300 K. Therefore a significant admixture of the $4f^6$ state to the $4f^7$ ground state can be excluded. Thus, from the Mössbauer point of view we have clear indications of a stable divalent ground state in EuCuP and EuAuP.

In the following we want to discuss the susceptibility data with respect to possible valence instabilities in our Eu compounds. It is well known that, very often, for an integral-valence RE ion the experimental values of the effective moment as deduced from paramagnetic susceptibility deviate from those calculated from Hund's rules. Such

a difference may be due to either experimental uncertainties, temperature-dependent interactions of the magnetic moments or a slight deviation from LS coupling, varying from system to system. Therefore, the effective moments derived from susceptibility data are not a good measure for the valence. Nevertheless, if one takes the values of p_{eff} (table 1) seriously, they give an estimation of about 2.07 for the Eu valence. This is still much less than those obtained from L_{III} XAS (see below).

Magnetic ordering alone does not exclude valence fluctuations. A coexistence of magnetic order and valence fluctuation may be possible, if the fluctuation energy at low temperatures becomes smaller than the magnetic ordering temperature (e.g. in the Eu(Pd, Au)$_2$Si$_2$ series [26]). Nevertheless, the paramagnetic susceptibility data in connection with the magnetic order give an argument for integral valence. The deviations of the susceptibility from an ideal Curie law $\chi = C/T$ are described by the Curie–Weiss law

$$\chi = \frac{C}{T - \Theta_{CW}} = \frac{C}{T - (\Theta_{mag} - T_{fluct})}.$$

Here, the Curie–Weiss temperature Θ_{CW} is the difference between the valence fluctuation temperature $T_{fluct} \geqslant 0$ [21], and Θ_{mag}, representing magnetic correlations; Θ_{mag} is usually negative for antiferromagnetic and positive for ferromagnetic order. Therefore, without valence fluctuation ($T_{fluct} = 0$) the susceptibility is enhanced for ferromagnetism and reduced for antiferromagnetism. The valence fluctuation results in a reduction of the susceptibility. However, the measurements on all our systems show an enhanced susceptibility compared to the Curie susceptibility of the free Eu^{2+} ion at low temperatures, up to at least three times the ordering temperature. This clearly excludes any valence fluctuation in the antiferromagnetic (and metamagnetic) compounds. For an ideal ferromagnetic system, Θ_{mag} is expected to be equal to the Curie temperature T_C, i.e. $\Theta_{CW} = T_C$. In our ferromagnetic systems Θ_{CW} is even larger than T_C, resulting in a further enhancement of the susceptibility and again excluding valence fluctuations. In fact, this observed enhancement of the susceptibility is a strong argument against valence fluctuation in all Eu compounds discussed here.

3.2. Valence determination from L_{III} XAS measurements

The above discussion shows that it is highly unlikely that Eu in these 1–1–1 compounds is not divalent. In spite of the observed double-peak structure even the XAS measurements give some indirect indication of a stable divalent Eu ground state. First, the double-peak structure is temperature independent while, in the model of interconfigurational fluctuations, a temperature dependence is usually expected [21, 27]. Second, the energy separation ΔE between the two absorption maxima is relatively large (more than 8 eV). In the mixed-valence compounds EuPdAs and Eu(Ni, Pd, Pt)P this energy separation is smaller than 8 eV. If we compare these values for ΔE with those of the alloy series EuPd$_{2-x}$Au$_x$Si$_2$ [1], the 1–1–1 compounds correspond to those on the gold-rich side ($x \geqslant 0.5$) that are shown to be divalent from Mössbauer effect, lattice constants and susceptibility [28].

Because of this evidence for divalent Eu we have to look for another interpretation of the double structure in the XAS spectra. The simplest explanation is impurities. Here, it should be mentioned that the Mössbauer measurements were performed on the same absorbers *after* the XAS measurements. From the absence of an Eu^{3+} line in Mössbauer spectroscopy a significant oxidation of the samples can be excluded. Even if one takes into account the higher sensitivity of the XAS measurements compared to the Mössbauer spectroscopy on

ionic compounds like Eu_2O_3 [29], the intensity of the 'trivalent' peak should not exceed $\sim 6\%$†.

Excitonic effects can be excluded, in metallic samples ($\rho < 1\,m\Omega$ cm), as the origin of the 'trivalent' peak that is often seen in insulators. A further explanation could be a multiple-scattering XANES structure. Therefore we performed XANES measurements on isostructural NdPdAs and SmPdAs compounds, too. There was no such structure around $8\,eV$, not even after scaling the spectra with the $Er^2 = $ constant law [30].

Since there is no satisfying interpretation of the XAS spectra in the 'single-particle' picture, we have to conclude that this picture fails in the case of the divalent 1–1–1 Eu compounds. Accordingly, the high-energy peak must be a 'shake-up' peak: after the creation of the 2p core hole in the fully relaxed final state the number of 4f electrons is lowered with respect to that of the undisturbed ground state due to the partial promotion of a 4f electron into the conduction band. The same conclusion was drawn by Wortmann [1] in the case of $EuPd_{2-x}Au_xSi_2$ and other Eu compounds and by Sampathkumaran and co-workers [5] in the case of $EuPd_2P_2$.

3.3. Comparison with related systems: $EuPd_2P_2$

We now want to compare the validity of our conclusion about the Eu valence in Eu(Cu, Ag, Au)(P, As, Sb) with that of the typical case of $EuPd_2P_2$ [5]. In all of these substances the 'L_{III} valence' amounts to about 2.15. However, the 'trivalent' line in $EuPd_2P_2$ is only shifted by $7.7\,eV$, while those in the 1–1–1 compounds are shifted by more than $8\,eV$. Since a larger energy separation corresponds to a stronger divalence [1], the 1–1–1 compounds are 'more divalent' than $EuPd_2P_2$. The same conclusion can be drawn from the Mössbauer isomer shift, which was only $-9.73\,mm\,s^{-1}$ in $EuPd_2P_2$ compared to about $-11\,mm\,s^{-1}$ in the 1–1–1 compounds.

The lattice constants are a clear indication of divalent Eu in the 1–1–1 compounds, while the only reliable conclusion from the volume anomaly of $EuPd_2P_2$ in the $REPd_2P_2$ series is that Eu is *not trivalent*. The volume anomaly of $EuPd_2P_2$ is even smaller than the volume anomalies of other divalent Eu compounds in $ThCr_2Si_2$ structure [24]. This observation first led Jeitschko and Hofmann to the suggestion that Eu is intermediate valent in $EuPd_2P_2$ [24]!

Only the larger magnetic moment of $EuPd_2P_2$ ($8.0\mu_B$, [6]) compared to those of the 1–1–1 compounds indicates a stronger divalence of $EuPd_2P_2$. However, as discussed above, the values of magnetic moments are slightly ambiguous. In general, an exact agreement of the measured magnetic moment with the theoretical value is more the exception than the rule. If we compare the absolute values of the susceptibility instead of its temperature dependence (i.e. the effective moments), we find a reduced susceptibility for $EuPd_2P_2$ ($\Theta_{CW} = -30\,K$ [6]), but enhanced values for the 1–1–1 compounds ($\Theta_{CW} > 0$), again indicating less instability of the 4f moment in the latter compounds. Finally, all compounds order magnetically; the ordering temperatures are of the same order of magnitude. The exact value for each compound is mainly determined by volume effects and not by valence fluctuations. From these facts it is clear that the 1–1–1 compounds are 'at least as divalent as' $EuPd_2P_2$, i.e. the $4f^7$ electron in the former compounds is as localized as that in the latter.

Finally, we want to discuss the conditions of occurrence of the 'shake-up' peak in L_{III} XAS measurements on Eu compounds. There are no, or at least much smaller, 'shake-up' peaks in the clearly divalent non-metallic compounds, e.g. EuO [31] and EuF_2 [1].

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† The higher L_{III} valence of EuAuP compared to EuCuP in spite of the more negative isomer shift may be caused by 2–3% of Eu_2O_3, undetectable in x-ray diffraction and Mössbauer effect measurements.

On the other hand, the metallic divalent Eu compounds in $ThCr_2Si_2$ structure that show final-state effects are on the verge of valence instabilities [1]. This is also true for the 1–1–1 compounds: in the phosphides the substitution of the noble metals Cu, Ag, Au by their neighbouring elements Ni, Pd, Pt leads to unstable-valence compounds as reported elsewhere [11, 13, 14]. The systematic variation of the occurrence of valence instabilities is a clear hint of the importance of the d band of the transition metal. This last point has been recently discussed in connection with valence-unstable EuPdAs [15].

4. Conclusion

We have shown that Eu in the nine compounds Eu(Cu, Ag, Au)(P, As, Sb) is nearly divalent. This conclusion was drawn from Mössbauer effect, lattice constant and magnetic susceptibility measurements. The double structure of the L_{III} absorption edge, which is usually taken as indication of a mixed-valence Eu, is caused by a final-state ('shake-up') effect. The occurrence of 'shake-up' effects seems to be a precursor of valence instabilities.

Acknowledgments

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