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1990 J. Phys.: Condens. Matter 2 7679

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Valence states in Eu/Pd and Eu/Ta interfaces

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Received 23 April 1990

Abstract. X-ray photoemission measurements have been performed on the Eu/Pd and Eu/Ta systems. Small amounts of Eu, $\sim 0\text{--}10 \text{ \AA}$, were evaporated on polycrystalline substrates of Pd and Ta. Eu was found to form overlayers on Ta, whereas on Pd a mixed interface layer was observed. Europium is always divalent on Ta, whereas both divalent and trivalent Eu were observed in the Eu–Pd interface, the $2+/3+$ intensity ratio being dependent on the amount of deposited Eu. A situation of inhomogeneous mixed valence, in which divalent and trivalent Eu ions occupy different sites, exists in the interface. The Eu atoms at the surface were always found to be divalent.

1. Introduction

The proximity of the 4f levels to the Fermi level in metallic rare earth materials facilitates several possible 4f counts in systems based on Ce, Sm, Eu, Tm, and Yb. Dependent on chemical environment, the lowest energy state may be one that favours 4f occupancy to valence band occupancy, or vice versa. If the 4f level overlaps the Fermi level, a situation of homogeneous mixed valence may occur [1], in which the 4f count is non-integer. In that case, the system fluctuates between two iso-energetic configurations on the time scale of the valence fluctuation time ($\sim 10^{-12}$ s) [1]. This work considers Eu in which the valence may be $2+$ (seven f electrons) or $3+$ (six f electrons), or may span the entire region in between (mixed valence). Examples include Eu metal and EuPd_2 ($2+$), EuPd_3 ($3+$), and EuCu_2Si_2 ($2.35+$) and EuRh_2 ($2.8+$) [1–3].

Since the coordination number at the surface is smaller than in the bulk, the valence at the surface of rare earth metals may be different from the bulk valence. Johansson [4] has calculated surface valence states for the rare earth elements, and he found that a divalent surface is more favorable than a divalent bulk. Photoemission experiments have shown that Sm, which is trivalent in the bulk, is divalent at the surface [5, 6]. Europium metal is divalent in the bulk as well as on the surface. However, intermetallic compounds based on Eu may be trivalent in the bulk. For instance, EuPd_3 is trivalent in the bulk, and has been argued to be divalent at the surface [7, 8].

Recent measurements where rare earths are deposited on various metal substrates, have shown that thin interface alloys frequently form at room temperature [9–12]. We have studied the Eu/Ta system in which overlayer growth is observed, and the Eu/Pd system in which formation of a thin, mixed interface alloy is seen, when Eu is deposited at room temperature. Studies of sputtered amorphous Eu–Pd alloys [13, 14] report a mixture of divalent and trivalent Eu sites in the bulk, frequently referred to as

inhomogeneous mixed valence. In the present work, we have studied europium valence states in the surface/interface regions, for small amounts of Eu on Pd and Ta by use of x-ray photoelectron spectroscopy.

2. Experimental

X-ray photoelectron spectra (XPS) were recorded by use of a hemispherical electron energy analyser, HA-50, Vacuum Science Workshop (VSW). Electrons were detected in a cone of a few degrees around an angle of near 45 degrees with respect to the surface normal. The x-rays were obtained by use of a twin anode (Al/Mg) source from VSW. A total energy resolution of about 1 eV was obtained. A Ta foil that could be cleaned by flash heating to elevated temperatures, was used as substrate. The Pd samples were produced by evaporating Pd films of thickness ~ 100 Å onto the Ta substrate. The Ta substrate as well as the Pd films were polycrystalline in nature. Both Pd (99.99% from Alfa products) and Eu (99.99% from Johnson Matthey) were evaporated from tungsten baskets that were thoroughly outgassed prior to the experiment. Evaporation rates were estimated by monitoring the attenuation of Ta substrate peaks. The Ta foil was mounted on a cryostat that could be cooled by liquid nitrogen to obtain temperatures near 80 K. The samples could be annealed by passing current through the Ta foil, and annealing temperatures were measured by optical pyrometry. The base pressure in the vacuum chamber was in the low 10^{-10} Torr range. Small traces of oxygen, $<5\%$, were always present on the Eu samples, but were thought to be too small to influence Eu core levels appreciably.

3. Results

X-ray photoemission results on the Eu/Ta and Eu/Pd systems at room temperature, as well as results after annealing of a Eu/Pd sample at temperatures up to 1000 K, are presented in the following.

3.1. Eu on Ta: overlayer growth

The attenuation of Ta 4f peaks follows an exponential relationship with the amount of deposited Eu. This observation together with the absence of Ta core level shifts, indicates overlayer growth of Eu on Ta at room temperature, as may be expected on a refractory metal. Europium $3d_{5/2}$ XPS spectra are shown in figure 1 for various low Eu depositions on Ta. The main peak near a binding energy of 1127 eV corresponds to Eu in its divalent state, and is often referred to as the 'well screened' peak. The high-binding-energy peak near 1134.5 eV, often referred to as the 'poorly screened' peak, may have three different origins. First, it may be due to traces of trivalent oxide, Eu_2O_3 , on the surface. Second, it may be due to trivalent Eu atoms in their metallic state. Finally, and most likely, the peak may be caused by a final state shake-up excitation.

Since the intensity of the 'poorly screened' peak increases with Eu deposition, a contribution from oxide on the surface is unlikely. Surface oxide is expected to be more important for low amounts of Eu on the surface, simply due to a larger surface/volume ratio. Elemental europium is divalent in the metallic state, and any trivalent metallic emission would have to be caused by Eu-Ta interactions, which would have made the

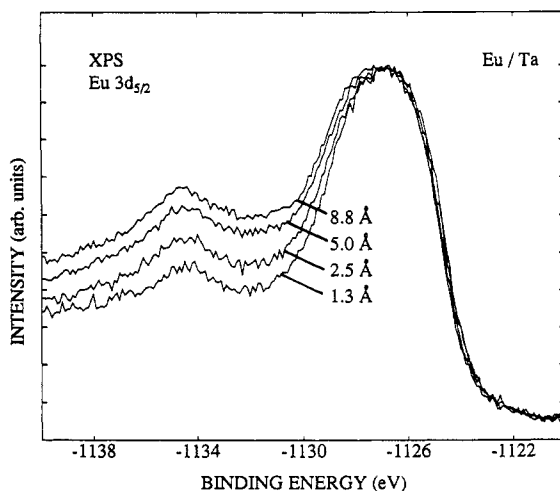


Figure 1. Eu 3d core levels for various small amounts, as indicated, of Eu on Ta. The smaller peak to higher binding energy correspond to an $f \rightarrow d$ shake-up excitation.

'poorly screened' peak more intense for lower Eu depositions. Based on the above considerations, we feel confident that the smaller peak in the Eu 3d spectra is caused by a final state shake-up process of the following type: $3d^{10}4f^7[ds]^2 \rightarrow 3d^94f^6[ds]^4 + e^-$, in which the final state in the photoemission process contains one less 4f electron. The extra conduction electron in the final state is brought in to neutralise the Wigner-Seitz cell. In this final state, the screening of the 3d core hole is poorer as compared to the direct photoemission process, due to one less localised 4f electron, and the corresponding peak appears at about 7.5 eV higher binding energy. Final state shake-up satellites have previously been reported in XPS from Eu metal [8].

3.2. Eu on Pd: interface formation

Indications of formation of a mixed Eu-Pd interface when Eu is evaporated onto a Pd film are threefold. Pd substrate peaks are attenuated less than would be expected from overlayer growth. Also, distinct shifts, up to ≈ 0.6 eV to higher binding energy, are observed in the Pd substrate peaks as Eu is deposited; figure 2. Finally, the Eu 3d peak positions are different, ≈ 0.7 eV to lower binding energy, from those observed on the Ta substrate; figure 3. A simple method [9, 11], in which formation of a homogeneous, mixed interface layer is assumed, estimates an average Eu volume fraction of about 70% in the interface. More realistically, a concentration gradient is expected to be present across the very thin interface.

Initially, for low Eu depositions up to ≈ 2.5 Å, the relative intensity of the 'poorly screened' Eu 3d photoemission peak increases with increasing Eu amounts; figure 4(a). Subsequently, for depositions above ≈ 2.5 Å, the relative intensity of the peak decreases; figure 4(b). The 'poorly screened' peak stems from metallic Eu ions in their trivalent state in the Eu/Pd system. The initial increase and subsequent decrease of intensity cannot be explained by a contamination feature nor by a shake-up excitation. However, a small contribution to the intensity from such effects cannot be ruled out. For low Eu depositions on Pd, some of the Eu atoms have a coordination of Pd atoms in such a way

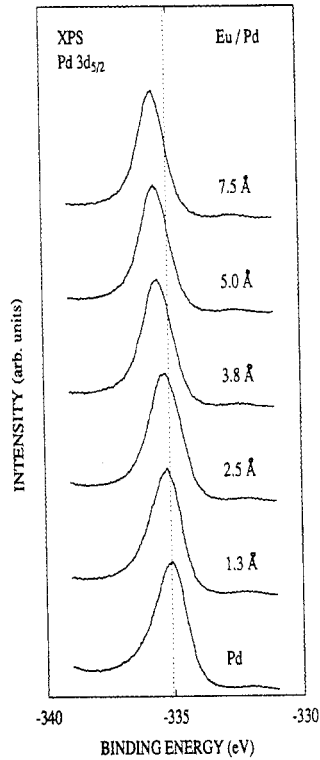


Figure 2. Pd core levels for various small Eu depositions, as indicated in the figure, on Pd. The shifts to higher binding energies are caused by alloying between Eu–Pd in a thin interface layer.

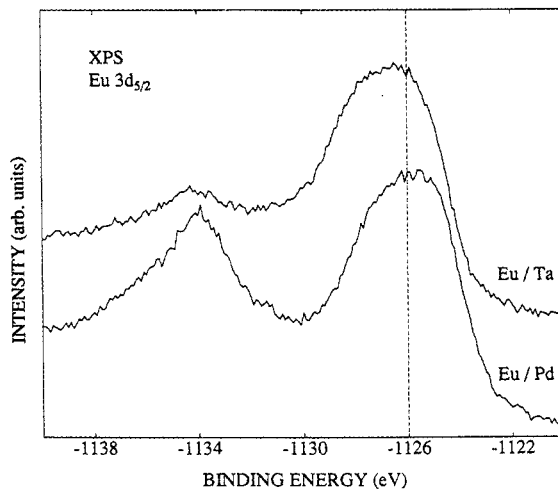


Figure 3. Eu 3d core levels for 2.5 Å Eu on Ta and Pd, as indicated.

that they favour the trivalent state. Most of the atoms are still divalent, as witnessed by the XPS spectra; figure 4. When more europium is deposited, the coordination is such that the divalent state is preferred by more of the Eu ions.

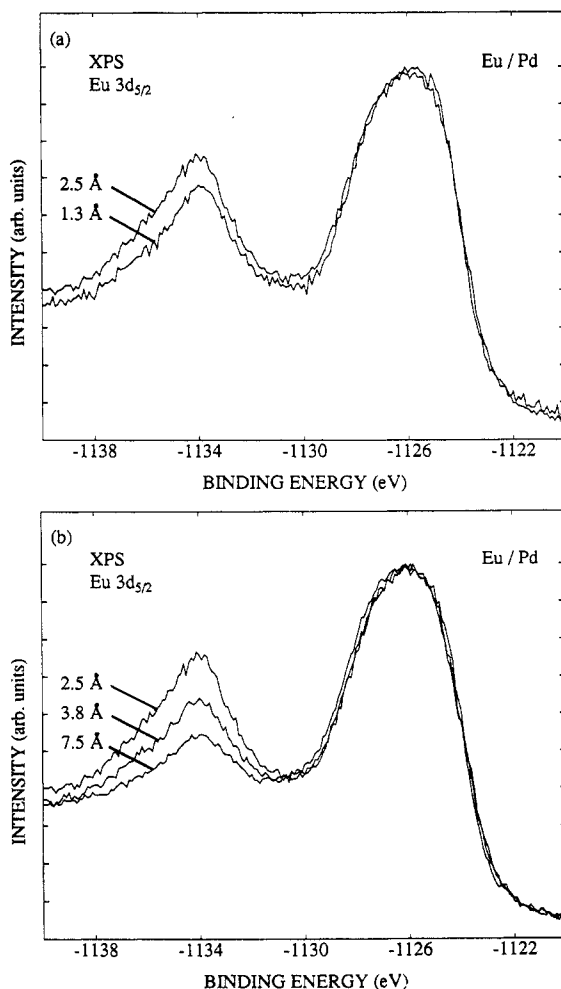


Figure 4. Eu 3d core levels for various Eu depositions on polycrystalline Pd. Spectra corresponding to effective Eu coverages as indicated, are displayed: (a) 1.3 and 2.5 Å, (b) 2.5, 3.8 and 7.5 Å.

The sample that corresponds to 2.5 Å Eu/Pd was cooled to ≈ 80 K in order to see if the larger divalent ions could be squeezed into the smaller trivalent state. No changes in the xps spectra were seen in going from room temperature to liquid nitrogen temperature, which is consistent with the interpretation that homogeneous mixed valence does not exist in the interface, but rather an inhomogeneous situation in which divalent and trivalent Eu atoms occupy different sites.

3.3. Annealing of the Eu/Pd system

In figures 5 and 6 are shown Eu and Pd 3d_{5/2} XPS spectra, respectively, after annealing of an 8.8 Å Eu/Pd sample at temperatures up to 1000 K. The Eu spectrum after annealing at 750 K for 10 seconds, figure 5, quite closely resembles that of EuPd₃ [8], and it is

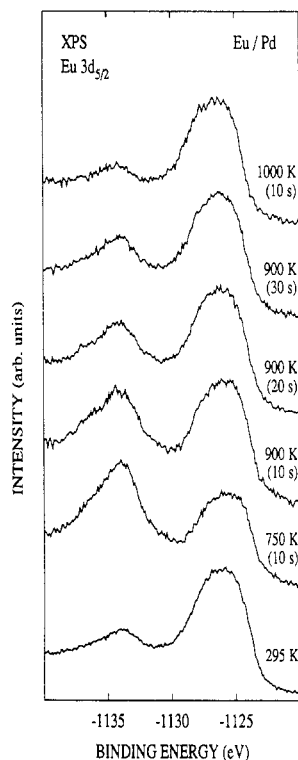


Figure 5. Eu 3d core levels from an annealed 8.8 Å Eu on Pd sample. The 750 K spectrum closely resembles previously published spectra from the intermetallic compound EuPd_3 [8], whereas the top spectrum (1000 K) may correspond to the divalent intermetallic compound EuPd_2 .

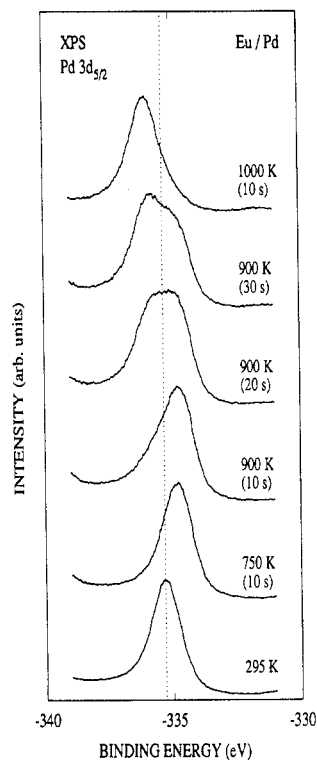


Figure 6. Pd 3d core levels corresponding to the Eu 3d spectra in figure 5.

conceivable that this intermetallic compound has formed at this temperature. The Pd $3d_{5/2}$ emission consists of one relatively sharp feature at this stage; figure 6. After annealing at 900 K, the 'poorly screened' peak decreases, and eventually, after annealing at 1000 K, the peak is as small as we ever observed in an Eu/Pd interface.

The evolution of the Pd 3d emission when the sample is annealed, is quite interesting. After annealing at 750 K the peak shifts about 0.5 eV to lower binding energy. At this point, the Eu–Pd interface, presumably, has formed the intermetallic compound EuPd_3 . When the sample is annealed at 900 K, the Pd $3d_{5/2}$ emission splits into two peaks, probably indicating the presence of at least two intermetallic phases in the interface. Upon annealing at 1000 K, only the one peak is present, and it is shifted about 1.1 eV to higher binding energy as compared to the 750 K sample; figure 6. At this stage the divalent compound EuPd_2 may have formed. The Eu/Pd intensity ratio is consistent with this conjecture.

4. Discussion

The increased intensity of the shake-up satellite ('poorly screened' peak) in the Eu 3d level for larger amounts of Eu on the Ta substrate, indicates that Eu–Eu interactions

are important for an $f \rightarrow d$ shake-up transition in europium. When Eu–Ta bonds form, the symmetry of the unfilled portion of the d band may be such that the $f \rightarrow d$ transition probability is lower as compared to the case of formation of Eu–Eu bonds. The presence of Ta 5d electrons, presumably, leads to an increased filling of the d-symmetric part of the conduction band, and a reduced $f \rightarrow d$ shake-up probability. Shake-up excitations in the Eu/Pd system could not be observed due to the presence of trivalent Eu ions. However, the almost filled Pd 5d band may cause quenching of $f \rightarrow d$ transitions when Eu–Pd bonds are formed, due to low density of unoccupied states of d symmetry above the Fermi level.

The ratio of trivalent/divalent Eu atoms, as estimated from the ‘poorly screened’/‘well screened’ intensity ratio, varies with the amount of Eu deposited on the Pd substrate. Initially, for effective Eu depositions up to about one monolayer, the number of trivalent Eu ions increases with Eu deposition. This evaporation regime, presumably, correspond to a situation where Eu and Pd mix in such a way so that the Pd coordination surrounding some of the Eu ions favours a trivalent ground state. Subsequently, for larger evaporations, fewer Pd atoms are located at the surface, and most Eu ions are in their divalent state. Therefore, the ‘poorly screened’ peak is relatively less intense than the ‘well screened’ main Eu $3d_{5/2}$ peak. The observation that the majority of the Eu atoms are divalent for all Eu evaporations at room temperature, supports a picture in which Eu ions are always divalent at the surface of the Eu/Pd system. The local environment around the trivalent Eu ions are believed to be near that in EuPd_3 . However, since the thin Eu–Pd interface is formed at temperatures that are well below those where nucleation and crystalline growth occur, the interface is likely to be amorphous.

The maximum number of trivalent Eu ions could be obtained by annealing at ≈ 750 K for a short period of time. This procedure results in a Eu 3d spectrum which is virtually identical to previously published spectra from the trivalent (in the bulk) intermetallic compound EuPd_3 [8]. The Eu atoms at the surface are also divalent in this compound. The absence of a temperature dependence on the $3+/2+$ intensity ratio may suggest that no homogeneously mixed valent Eu atoms are present in the Eu–Pd interface, which means that the Eu 4f levels do not overlap the Fermi level, and no valence fluctuations can occur. Some caution should be employed, however, considering that there are examples of mixed valent Eu systems in which a temperature change from 300 to 80 K does not change the valence appreciably [1, 2].

5. Summary

Europium overlayers on Ta and Pd have been studied by x-ray photoelectron spectroscopy. Eu forms overlayers on Ta, whereas on Pd, mixed interface layers are observed. The Eu ions are always divalent on Ta, where an $f \rightarrow d$ shake-up satellite peak was observed. Eu ions were found to be trivalent as well as divalent in the Eu–Pd interface layer, but the ions at the surface are always divalent due to the lower coordination number. A situation of inhomogeneous mixed valence exists, in which divalent and trivalent ions occupy different sites.

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