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Photoemission studies of Eu–Rh and Eu–Pd interfaces

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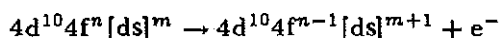
Abstract. Photoemission studies using synchrotron radiation, as well as a laboratory x-ray source, have been performed on Eu/Rh and Eu/Pd overlayer systems. Europium was deposited at room temperature onto evaporated films of Rh and Pd. Substrate core level attenuation curves, as well as shifts in substrate peak positions upon Eu deposition, suggest the formation of interfacial alloys even at room temperature. Eu 4f states were studied by resonant photoemission, which showed the Eu to be divalent at the surface. Constant final state (CFS) measurements revealed the presence of trivalent Eu below the surface.

1. Introduction

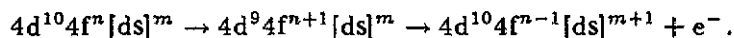
Materials based on rare earth metals exhibit a large variety of physical properties, and are widely used in industrial applications, e.g. permanent magnets and electronic devices. Of particular interest, from a fundamental point of view, are the elements Ce, Sm, Eu, Tm and Yb, which may exist in different valence states, including valence unstable states [1] in which the rare earth ion may be characterized by a non-integer number of 4f electrons. The present photoemission study considers vapour deposited Eu films on substrates of Rh and Pd. All three possible types of 4f electron configurations are present in the bulk of Eu–Rh and Eu–Pd compounds: (i) trivalent compounds, e.g. EuPd_3 , (ii) homogeneous mixed valent compounds, e.g. EuRh_2 , and (iii) divalent compounds, e.g. EuPd_2 . The situation is made more complicated by the tendency of Eu compounds to favour divalency at the surface [2], when using surface sensitive probes; for instance, whereas the Eu valency in the bulk of EuPd_3 is 3+, the surface valency is 2+ [3, 4].

Recent experiments have shown that interfacial alloys are formed when various rare earth elements are deposited at ambient temperatures onto a number of different substrates [5–11]. The interface alloys are thought to be amorphous in nature, since they form at temperatures which are well below those where nucleation and crystalline growth are expected to occur [9]. In the present work, we study electronic states and composition of the mixed interface. The Eu valency is sensitive to the chemical environment, and the distinct differences in 4f emission from divalent and trivalent species, make 4f emission a useful means of studying these interfaces. Eu 4f photoemission was enhanced (suppressed) by tuning the photon energy to the Fano resonance energy of 141 eV (off-resonance energy of 133 eV). In this energy region the photo-ionization cross-sections of the transition metal 4d states are small due to

the proximity to the Cooper minimum. The giant resonance of 4f emission comes about due to a quantum interference between direct photoemission [12]:



and the super-Coster-Kronig decay of an intermediate state:



The number of conduction electrons [ds] is given by the requirement of maintaining charge neutrality in the Wigner-Seitz cell. 4f electrons which are emitted at this photon energy are extremely surface sensitive, and almost the entire signal may be considered to originate from the topmost couple of atomic layers. Less surface sensitive data were obtained by recording constant final state (CFS) scans. In this mode, the photon energy is varied and secondary electrons are recorded at constant kinetic energy. The probing depth is in this case typically of the order of 50 Å [13]. Information about 4f states was obtained by ramping the photon energy over the Eu 4d excitation threshold. Basically, this represents a measurement of the Eu $N_{IV,V}$ absorption edge.

2. Experimental details

Synchrotron radiation measurements were performed at beam line U7B at NSLS at Brookhaven National Laboratory, and x-ray photoelectron spectra (XPS) were recorded in the home laboratory. The beam line features a plane grating monochromator (PGM) which was used in conjunction with a double-pass cylindrical mirror electron energy analyser (CMA). A total energy resolution of about 0.5 eV was obtained at a photon energy of 120 eV. XPS measurements were done using a twin-anode x-ray source and a hemispherical electron energy analyser. Pd and Eu were evaporated from resistively heated tungsten baskets, whereas Rh was evaporated by passing the current through a thin Rh wire. Rh and Pd were evaporated onto a polycrystalline Ta foil, which was cleaned by flash-heating above 2000 °C. The base pressure in the vacuum chamber was about 5×10^{-10} Torr. Traces of contamination were observed in some of the spectra, but were small and not believed to affect the interpretation of the data. CFS measurements were performed by collecting electrons of kinetic energy 10 eV, with the analyser pass energy at 200 eV, to ensure high count rates and to reduce the possible influence of sharp photoelectron features in the spectra.

3. Results and discussion

Substrate core level XPS emission intensities were monitored as Eu was deposited on Rh and Pd. Figure 1 shows the attenuation of Pd (upper panel) and Rh (lower panel) 3d photoemission plotted versus Eu evaporation time. The Eu evaporation rate was about 2.5 \AA min^{-1} . The dotted curves show the exponential attenuation, which would be expected to result from even overlayer growth. The deviation of the data points from these lines suggests the possible clustering of the adlayer or the formation of interfacial alloys or compounds. This type of data can be used to obtain more information about the morphology of rare earth-transition metal interfaces. The full

curves in figure 1 represent a simplistic model in which formation of a homogeneous mixed interface alloy is assumed [6, 8], and in which the substrate core level intensity is given by:

$$I_{\text{substrate}} = (1 - \alpha) + \alpha \exp(-tr/\lambda\alpha)$$

where t and r are evaporation time (min) and rate ($\text{\AA} \text{ min}^{-1}$), respectively, and λ is the electron mean free path for the core level in question. The volume fraction, α , of Eu in the overlayer, in this model, was estimated to be 0.73 in the case of Pd and 0.92 in the case of Rh. As shown in figure 1, good fits to the data could be obtained by this simple model. Fits to another simple model, in which a constant concentration gradient across the mixed interface was assumed [8], are shown by dashed lines. The substrate emission intensity is in this model given by:

$$I_{\text{substrate}} = (\lambda/2tr)[1 - \exp(-2tr/\lambda)].$$

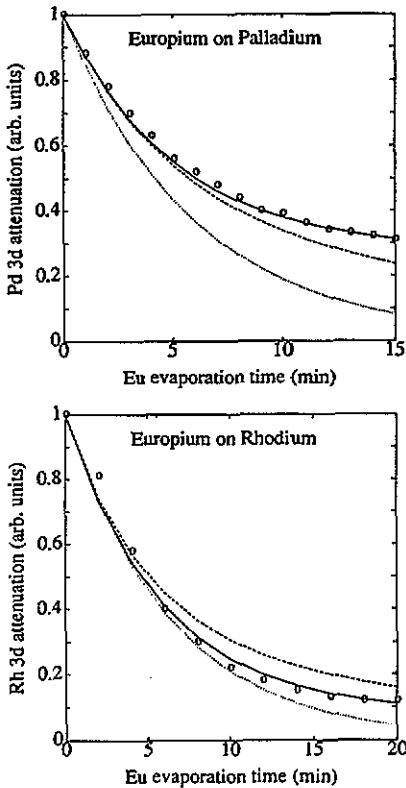


Figure 1. Attenuation of Pd (upper panel) and Rh (lower panel) 3d emission intensity (circles) as Eu is deposited at a rate of about $2.5 \text{ \AA} \text{ min}^{-1}$. The dotted curves show exponential decay, and the full and broken curves are fits to simple models as described in the text.

Clearly, this model does not fit the data well. Realistically, a varying concentration gradient may be expected across the interface. Still, the employed models are argued

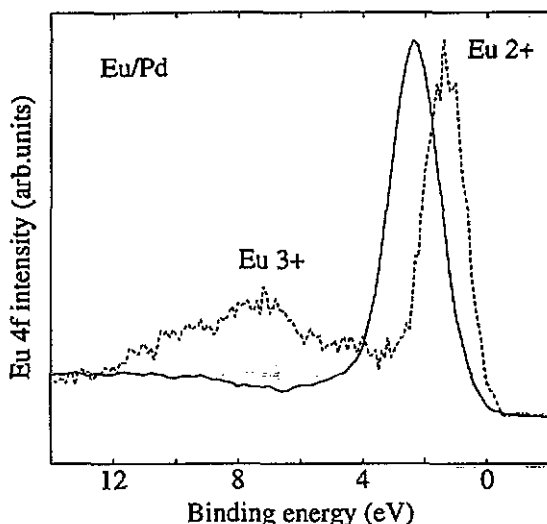


Figure 2. Resonant Eu 4f photoemission ($h\nu = 141$ eV) from a sample where about 35 Å Eu was deposited onto a Pd substrate. Full curve: as-deposited sample, broken curve: sample annealed at about 500 °C for one minute. The intensities have been scaled to be of the same overall heights. The contributions from di- and tri-valent Eu are indicated in the figure.

to lend support to the notion of a mixed interface. It is evident from figure 1 that the tendency for formation of an intermixed interface is stronger in the case of Pd as compared to Rh. This observation is consistent with the larger surface free energy [14] and melting temperature of Rh. The intermixed interfaces seem to extend over many atomic lattice spacings.

Divalent 4f emission in Eu may be described by the transition $4f^7(5d6s)^2 \rightarrow 4f^6(5d6s)^3 + e^-$, and trivalent 4f emission by $4f^6(5d6s)^3 \rightarrow 4f^5(5d6s)^4 + e^-$. The extra electron in the final states takes care of charge neutrality in the Wigner-Seitz cell. Photoemission from trivalent and divalent Eu can readily be separated from each other, even if the ground state energies of the trivalent and divalent Eu configurations are nearly the same, since screening of the core hole is strongly dependent on the number of 4f electrons. Divalent Eu, having one additional 4f electron as compared to trivalent Eu, provides better screening of the photo hole, and the 4f peak is observed about 2 eV below the Fermi level, whereas the trivalent emission is observed at about 6 eV higher binding energy.

Resonant 4f photoemission ($h\nu = 141$ eV) from Eu/Pd is shown in figure 2. About 35 Å of Eu was deposited at a rate of about 1.5 \AA min^{-1} onto a Pd substrate. The full curve shows the 4f spectrum of the sample as deposited, whereas the broken curve shows the spectrum after annealing to about 500 °C for one minute. The intensities have been scaled to be of the same overall height in figures 2–4. In reality, the Eu intensities are lower in the annealed samples. Only divalent Eu signal is observed in the full curve spectrum, whereas divalent as well as some trivalent signal is observed after annealing (the broken curve spectrum). The dominant trivalent 4f multiplet peaks of the mixed valent compound EuPd_2Si_2 at low temperature (valency of about 2.9+ for $T < 100$ K), have been reported near 6.6, 7.4 and 9.6 eV [15]. A distinct shift of about 1.1 eV, to lower binding energy of the divalent Eu 4f peak was seen after annealing. This shift as well as the presence of a trivalent 4f signal,

are indicative of formation of a trivalent Eu compound upon annealing, most likely EuPd_3 [10] or EuPd_5 [16]. The large divalent emission, presumably, results mainly from Eu ions that are located at the surface. In addition, divalent Eu may be present in the bulk in other Eu-Pd configurations than EuPd_3 . The fact that the dominant 4f emission is closer to the Fermi level for the annealed sample as compared to the as-evaporated sample, indicates that the annealed sample is nearer the valence unstable case, in which the 4f level is required to overlap with the Fermi level.

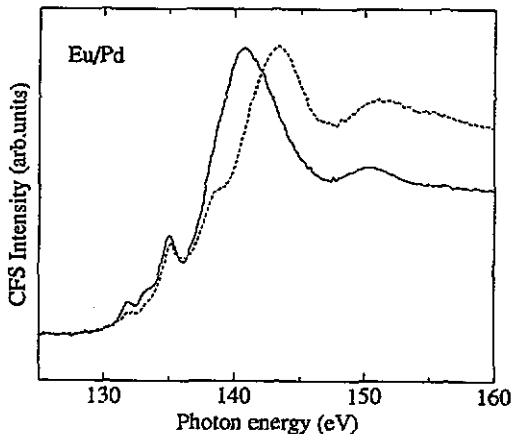


Figure 3. CFS scan in the region of the Eu 4d absorption threshold. The Eu/Pd specimens are the same as in figure 2. The intensities have been scaled to be of the same overall heights.

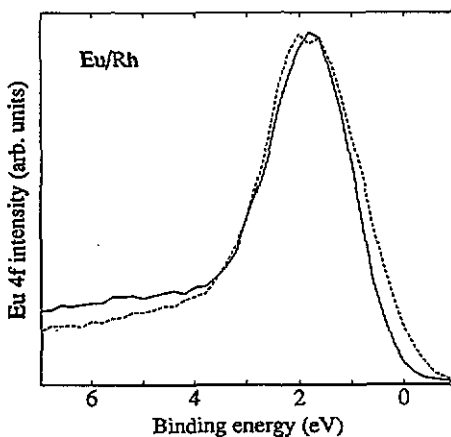


Figure 4. Resonant Eu 4f photoemission ($h\nu = 141$ eV) from a sample where about 35 Å Eu was deposited onto a Rh substrate. Full curve: sample as deposited, broken curve: sample annealed at about 500 °C for one minute.

Constant final state (CFS) spectra for the Eu/Pd system are shown in figure 3. The samples used are the same as in figure 2. The full curve represents the 'as-deposited' sample, and the broken curve is the annealed sample. The dominant features in the photoabsorption spectrum from divalent Eu may be identified by comparisons with the calculations by Sugar [17]. The feature in the CFS spectra that appears at a photon

energy of about 152 eV is assigned to trivalent Eu. The presence of a trivalent signal in the CFS spectrum of the as-deposited sample, and the absence of a trivalent signal in the more surface sensitive 4f emission spectrum (figure 2), show that the trivalent Eu is located below the topmost two or three atomic layers. The major feature in the spectrum from the annealed sample (broken curve, figure 3) is located about 2.5 eV to higher photon energy with respect to the major feature in the spectrum from the as-deposited sample (full curve, figure 3).

It should be noted that the presence of trivalent Eu in the as-deposited sample is inconsistent with non-reactive clustering of Eu on the surface, since Eu metal is always in its divalent valence state. Eu atoms at a surface, in all systems known to us, are always divalent. Further support of the notion of interfacial alloys is lent by the work of Butera *et al* [11] which clearly shows that intermixing takes place in the Ce/Ge(111) and Ce/Si(111) overlayer systems. Finally, distinct substrate core level shifts, were observed previously as Eu was deposited on Pd [10] and Rh [18] at room temperature, are indicative of interfacial alloy formation.

The observed substrate core level attenuation profiles may also most probably be reasonably well described by models of clustering or island formation on the surface. As pointed out above, clear evidence for reactive interface formation from observation of electronic states and core level shifts rules out an explanation based on clustering or island formation alone. However, we cannot rule out the possible presence of some tendency of clustering on the surface in addition to the observed formation of a mixed interface. Unfortunately, we lack experimental data for a good description of the nature or smoothness of the Eu film.

The europium 4f emission becomes slightly broader upon annealing of the Eu/Rh sample. The full curve in figure 4 shows the as-deposited sample, and the broken curve shows the sample after annealing at about 500 °C for one minute. About 35 Å of Eu was deposited at a rate of about 1.5 Å min⁻¹ onto a Rh substrate in this case. The divalent 4f emission was observed in the Eu/Rh system, even after annealing.

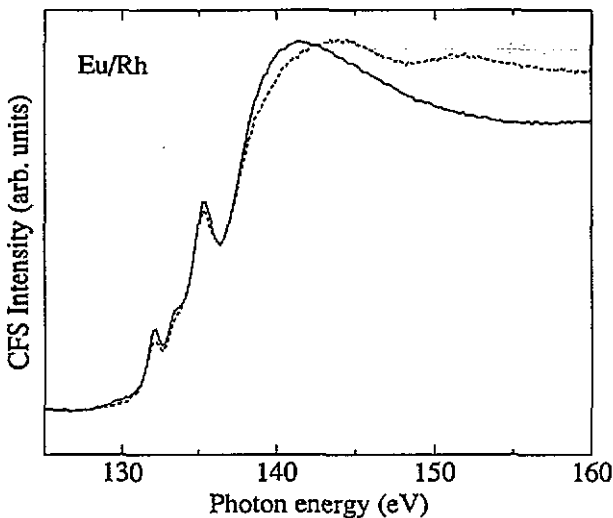


Figure 5. CFS scan in the region of the Eu 4d absorption threshold. The Eu/Rh specimens are the same as in figure 4.

The CFS spectra from the as-deposited (full curve) and annealed (broken curve)

Eu/Rh samples are shown in figure 5. The samples used are the same as in figure 4. The major peaks in these spectra are considerably wider than in the case of the Eu/Pd system (figure 3). The feature near 152 eV photon energy is clearly visible in the spectrum from the annealed sample, but not in the as deposited case. This indicates that at most a very tiny portion of the Eu is trivalent in the as deposited Eu/Rh sample. The mixed valent compound EuRh_2 (valency of about 2.8+ at room temperature [1]) is a likely candidate to form upon annealing. Again, the dominant feature in the annealed sample is located at about 2.5 eV higher photon energy, as compared to the as-deposited sample. The separation between the dominant feature and the 3+ peak at about 152 eV, is about 8 eV in both the Eu/Pd and Eu/Rh systems.

Previous XPS measurements reveal the presence of trivalent Eu states in as-deposited (at room temperature) Eu on Pd [10] and Eu on Rh [18] systems. The 3+ emission is weaker in the Rh case. Absence of a 3+ signal in the resonant 4f photoemission data, figures 2 and 4, shows that only divalent ions are present in the top two or three atomic layers. Only a few trivalent intermetallic Eu systems are known to exist [16, 19], so trivalent emission from these interface systems are likely to originate from Eu ions where the local environments are similar to those of EuPd_3 or EuPd_5 and EuRh_2 for Pd and Rh, respectively. The actual compounds probably do not form, rather the local environment of Eu atoms may, in a narrow region of the interface, resemble that of a trivalent Eu compound, or Eu may just be in a dilute configuration that favours the trivalent state. As mentioned above, the interfaces in the case of the as-deposited samples, may not be crystalline in nature, since they form at relatively low temperatures.

4. Summary

We have observed intermixed interfaces to form when Eu is deposited at room temperature onto vacuum deposited substrates of Pd and Rh. This confirms previously obtained results on the Eu-Pd system. The extent of the interfaces are estimated to be many atomic lattice spacings. Surface sensitive photoemission shows that the outermost few atomic layers are divalent, whereas less surface sensitive CFS measurements reveal the existence of trivalent Eu ions in the as-deposited Eu/Pd sample. The fraction of trivalent Eu was found to increase with moderate annealing of the sample. In the case of Eu/Rh, a trivalent signal was only observed after annealing. It is evident from this study as well as from previous studies that resonant photoemission is a suitable tool for studying rare earth interfaces in systems where the rare earth cations may possess two different valence states. Future work on single-crystal substrates may be of interest to obtain further information on rare earth/transition metal interfaces.

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