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Evaporated Eu films were exposed to oxygen up to 100 L. Using novel techniques of photoelectron spectroscopy in connection with synchrotron radiation as a tunable light source we detect the presence of both Eu^{2+} and Eu^{3+} ions in the sample with a close correspondence to mixed valence Eu_3O_4. At elevated temperature (400°C) only Eu^{2+} is found.

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Among the rare earth compounds those in which the rare earth ions may occupy different valencies have attracted most attention. An interesting example out of this group of materials are the oxides of Europium. The monoxide EuO has a cubic NaCl-type structure, whereas the trivalent oxide Eu_2O_3 has an anisotropic monoclinic structure (see e.g. Ref. 1). Additionally Eu may form an oxide where both divalent and trivalent Eu ions exist, i.e. the mixed valence compound Eu_3O_4. This oxide has the $CaFe_2O_4$-structure where the cations with different valence occupy different lattice sites. Thus this compound contains no charge transfer contrary to most other mixed valence compounds.

We have studied the oxidation of in situ evaporated Eu films using synchrotron radiation induced photoemission. We find both valencies present in the oxidized sample; its electronic structure exhibits a close correspondence to the mixed valence oxide Eu_3O_4.

The measurements were performed in the Hamburger Synchrotronstrahlungslabor HASYLAB with the FLIPPER monochromator [3]. Details of the photoemission set-up are given in Ref. 4. High purity Europium (99.99 %) was evaporated under UHV conditions from tungsten baskets onto copper and stainless steel substrates. The clean metal surface was oxidized by exposure to high purity oxygen (99.9 %). Reference measurements on Eu_2O_3 were taken on a powder pressed into indium substrate under air. The exposure of these samples to atmospheric pressure does not mean a severe drawback since they contain Eu in its highest oxidation stage.

Energy distribution curves (EDC's) at 40 eV photon energy taken for different oxygen exposures are displayed in Figure 1. The 4f emission of the divalent Eu ions in the metal at 2 eV binding energy[5] has a counterpart in the spectra of the oxidized samples which decreases in intensity with increasing exposure but still persists at 100 L. The main features for the oxidized samples occur between 4 eV and 12 eV binding energy. The spectrum of the clean metal also shows weak structures in this energy range but we are unable to judge whether these are due to the clean metal or to sample impurity since only 0.1 L of oxygen exposure enhances the intensity of these structures by at least a factor of 2 (compare also Ref. 5).

The valency of the Eu ions can be deduced from the multiplet splitting which the photoionized 4f shell exhibits in the EDC's. In terms of LS coupling the 4f ionization can be written as $(f^7)^8S \rightarrow (f^6)^7F + e^-$ for divalent Eu, $(f^6)^7F \rightarrow (f^5)^6H, {}^6F, {}^6P + e^-$ for trivalent Eu with a multiplet splitting of about 4 eV[6]. For a comparison with the EDC's the 4f emission has to be disentangled from the emission of other valence orbitals which have mainly oxygen 2p character. This is usually done by tuning the photon energy and making use of the different energy dependence of the corresponding photoionization cross-sections. However, the correlation with the 4f occupation is much clearer for the 4d→4f resonance excitations which occur between 100 eV and 200 eV photon energy for the rare earths[7]. The strong exchange interaction between the 4d core hole and the open 4f shell spreads the excited $4d^9 4f^{N+1}$ configurations over an energy range as large as 10 - 20 eV[8]. The shape of the absorption spectrum in this energy region is specific for the ground state 4f occupation[7,8]. Since the photoelectric yield of scattered electrons with low kinetic energy is proportional to the total absorption we take constant final state (CFS) spectra for a final energy E_f of 5 eV. In this spectroscopic technique the energy of the electron analyzer is set to a constant value (E_f) while the monochromator tunes the photon energy. The result shown in Figure 2 immediately proves the change of the 4f occupation when the divalent Eu ions of the metal are exposed to oxygen. It does, however, not exclude a mixture of divalent and trivalent Eu ions in the oxidized sample for which the EDC's in Figure 1 provided some evidence.

To investigate this question further we introduce a third spectroscopic technique, constant initial state (CIS) spectroscopy. Here, the photon energy and the energy of the electron analyzer are tuned synchronously so that we follow the photoemission intensity of a structure at fixed binding energy as a function of the excitation energy. The key to the advantage of this technique is the intershell interaction between the 4d and 4f excitations: The 4f excitations are strongly coupled to the 4d→4f resonance absorption so that their energy dependence closely resembles the absorption profile[9]. Thus the photon energy dependence unambiguously links every 4f structure of an EDC to its original occupation number for which the resonance profile can be taken as a fingerprint. This technique has successfully been exploited to confirm the valence change at the surface of Sm metal[10], to investigate mixed valence SmB_6[11], and the oxygen induced valence change of Yb metal[12]. Applying this technique to the oxidized Eu sample we cannot only readily detect the presence of both valencies but also locate the corresponding 4f-emission in the EDC (see Fig. 3).

We note that also the structure at 5 eV binding energy (labelled O 2p in Fig. 3) shows a resonance enhancement but with a more symmetric resonance profile. Measurements on rare earth metals revealed that symmetric profiles can be expected for valence levels which are less localized than the 4f shell[9]. For 3d transition metal compounds a theoretical study showed that also ligand states participate in the 3p-3d resonances with the strength and the profile of the resonance interaction depending on the degree of 3d-ligand interaction[13]. These questions are beyond the scope of this paper; here we concentrate on the behaviour of the 4f emission.

Since the spectra show the persistence of divalent Eu ions even at 100 L oxygen exposure the chemical composition of the oxidized film needs further investigation. In view of the high reactivity of metallic Eu and the high surface sensitivity of photoelectron spectroscopy in this energy range it appears unlikely that the clean metal still contributes to the spectra. A mixture of divalent and trivalent oxide phases and/or the oxide Eu_3O_4 containing both valencies are the alternative explanations. Figure 4 contains the comparison between EDC's of EuO, Eu_2O_3, and the oxidized metal film, the monoxide spectrum is taken from Ref. 6. Since Eu_2O_3 showed severe charging its spectrum cannot be located relative to the Fermi energy. Therefore we cannot determine binding energies relative to a general reference level but only relative to the top of the valence band. We interprete the onset of the EDC of Eu_2O_3 as the top of the oxygen 2p-derived valence band. In Figure 4 this onset is aligned with the equivalent structure of the oxidized film. We cannot rule out an alternative interpretation of the onset of the EDC taken on Eu_2O_3 as due to f-emission from divalent Eu atoms which may be contained in our sample because of the applied preparation technique, although measurement at different photon energies let such an interpretation appear unlikely. In any case the conclusions derived from these measurements remain valid. We find distinct differences for the 4f-structures of the divalent and trivalent oxides compared to the oxidized film.

The results for the energy positions and the band widths are summarized in Figure 5. The quantitative determination of the binding energies and band widths of the Eu oxides makes use of both the general cross-section behaviour and the resonance interaction of the valence levels. The 4f emission can be compared with calculated 4f photoelectron spectra based on the intermediate coupling scheme[14]. The 4f binding energy corresponds to the binding energy at which the ground state of the ionized 4f shell is found. The large width of the 4f structures limits the accuracy of this determination. At low photon energies ($\lesssim$ 30 eV) the 4f emission is expected to be negligible because of its comparatively low cross-section[6,4] which allows the determination of the band width of the other valence orbitals.

In Figure 5 the 4f multiplet splitting is also indicated though somewhat simplified by use of LS terms only. For comparison corresponding results are included for EuO[15,6] and Eu_3O_4 [16]. While EuO was also investigated in photoelectron spectroscopy[15,6], for Eu_3O_4 only optical absorption measurements are available[16] which yield the binding energies of the 4f levels relative to the empty conduction bands of d symmetry provided that an interaction between the excited electron and the hole can be neglected.

For the 2p-bandwidths we find 3 eV in EuO [15], 9 eV in Eu_2O_3, and 8.5 eV for the oxidized film. The 4f ionization energies for the divalent Eu ions ($f^7 \rightarrow (f^6)\ {}^7F$) are 1.4 eV in EuO [15,6], and 1.85 eV for the oxidized film ; the 4f ionization potentials for the trivalent Eu ions ($f^6 \rightarrow (f^5)\ {}^6H$) are 5.4 eV below the top of the 2p-band in Eu_2O_3 and 3.6 eV below the top of the 2p-band in the oxidized film (7.45 eV below E_{Fermi}). Therefore, the oxidized film cannot be interpreted as a mixture of purely divalent EuO and purely trivalent Eu_2O_3. However, our sample shows an energy separation between the 4f ionization potentials of the divalent and trivalent Eu ions of 5.6 eV in close agreement with the value obtained for Eu_3O_4 [16]. The electronic structure of the oxidized Eu metal evidently exhibits a correspondence to that of the mixed valence compound Eu_3O_4.

Since the chemical preparation of mixed valence Eu_3O_4 is an extremely difficult task [2] our result provides useful information also about the chemistry of this compound. This aspect becomes even more dominant when the temperature of the oxidized Eu film is elevated above room-temperature. We see a continuous decrease of the photoemission intensity from the trivalent 4f states accompanied by a continuous increase of the divalent 4f emission (Fig. 6). At 400°C the spectrum closely resembles the structure of divalent EuO as deduced from Ref. 15. We note in particular that the maximum of the ^7F component is shifted by 0.3 eV towards lower binding energy in reasonable agreement with the lower 4f ionization potential of EuO compared to the oxidized film at room temperature (compare Fig. 5). The spectrum obtained at 400°C is preserved also if the temperature of the sample is lowered again.

Our results show some similarity to an earlier oxidation study of Eu [17]. In the previous work, EuO was obtained by evaporation of Eu metal in oxygen atmosphere onto a substrate heated to 400°C [17]. At lower temperature both Eu valencies were found in the oxide [17]. It must be pointed out, however, that the work reported in Ref. 17 was carried out in a UHV system with a base pressure of 10^{-7} Torr which is by far not sufficient to prepare clean Eu metal. The base pressure in our sample chamber was $1 \cdot 10^{-10}$ Torr.

Photoelectron spectroscopy probes electronic structures. Since for the Eu oxides no band structure calculations are available which relate the electronic structure to the lattice,[18] only indirect conclusions on the lattice structure of the oxidized film can be drawn. The stoichiometric ratio between divalent and trivalent Eu ions in the Eu_3O_4 lattice is 1 : 2 ($Eu^{2+}Eu_2^{3+}O_4$ [2]). The ratio between divalent and trivalent 4f emission in our spectra cannot accurately be determined because the emission of other valence orbitals partly overlaps, and because a surface shift might change this ratio at the surface [19]. The influence of both effects is smallest for high photon energies. For a 200 eV spectrum we estimate a value of 1 : 2.5 close to the 1 : 2 ratio for the Eu_3O_4 lattice.

For the difference between the 4f ionization energies we find a value of 5.6 eV in agreement with the optical measurements on Eu_3O_4 (5.7 eV [16]). This value is close to but still different from the Coulomb energy for which XPS measurements on the homogenous mixed valence compound $EuCu_2Si_2$ yield a value 6 - 7 eV [20]. Since the ionization energies depend on the chemical environment of the atoms an interpretation of this difference in terms of chemical shifts can trace it down to the different locations of the Eu ions in the Eu_3O_4 lattice. Here, the bond length of the divalent Eu ions to the neighbouring O ions is 2.711 Å while for the two trivalent Eu ions in the unit cell the bond lengths to the O ions are 2.337 Å and 2.343 Å, respectively [2]. Our data provide evidence that the 4f binding energy of the divalent Eu ions is lowered by 0.3 eV when going from Eu_3O_4 to EuO (bond length 2.57 Å [1]). Since the coordination number are equal in both cases [1,2] a chemical shift accounts quantitatively for the measured binding energies.

In conclusion we have shown that oxidized Eu films contain both divalent and trivalent Eu ions. The oxide that naturally contains both Eu valencies is $Eu^{2+}Eu_2^{3+}O_4$. We demonstrated that the electronic structure of our samples closely correspond to that of the mixed valence oxide even in those details which are related to the lattice structure.

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Figure Captions

Fig. 1 EDC's of clean and oxidized Eu metal. The intensities of the spectra are comparable.

Fig. 2 Yield spectra of clean and oxidized Eu metal taken at a final energy of 5 eV.

Fig. 3 Yield spectrum and CIS spectra taken for the 4f emission of the divalent and trivalent Eu ions of the Eu film exposed to 1L O_2. The initial energies of the CIS spectra are indicated in the EDC.

Fig. 4 Comparison between an XPS spectrum of EuO from Ref. 6 and EDC's of Eu_2O_3 and the oxidized metal taken at 100 eV photon energy. The Eu_2O_3 spectrum is aligned at the top of the valence band.

Fig. 5 4f-energy positions and band widths of different Eu-oxides. The results for Eu_2O_3 and Eu_3O_4 have been aligned in energy (see text), the location of the structures relative to the Fermi level is not known.

Fig. 6 EDC's of oxidized Eu metal at room temperature, at 300° C and 400° C. The intensities are comparable.

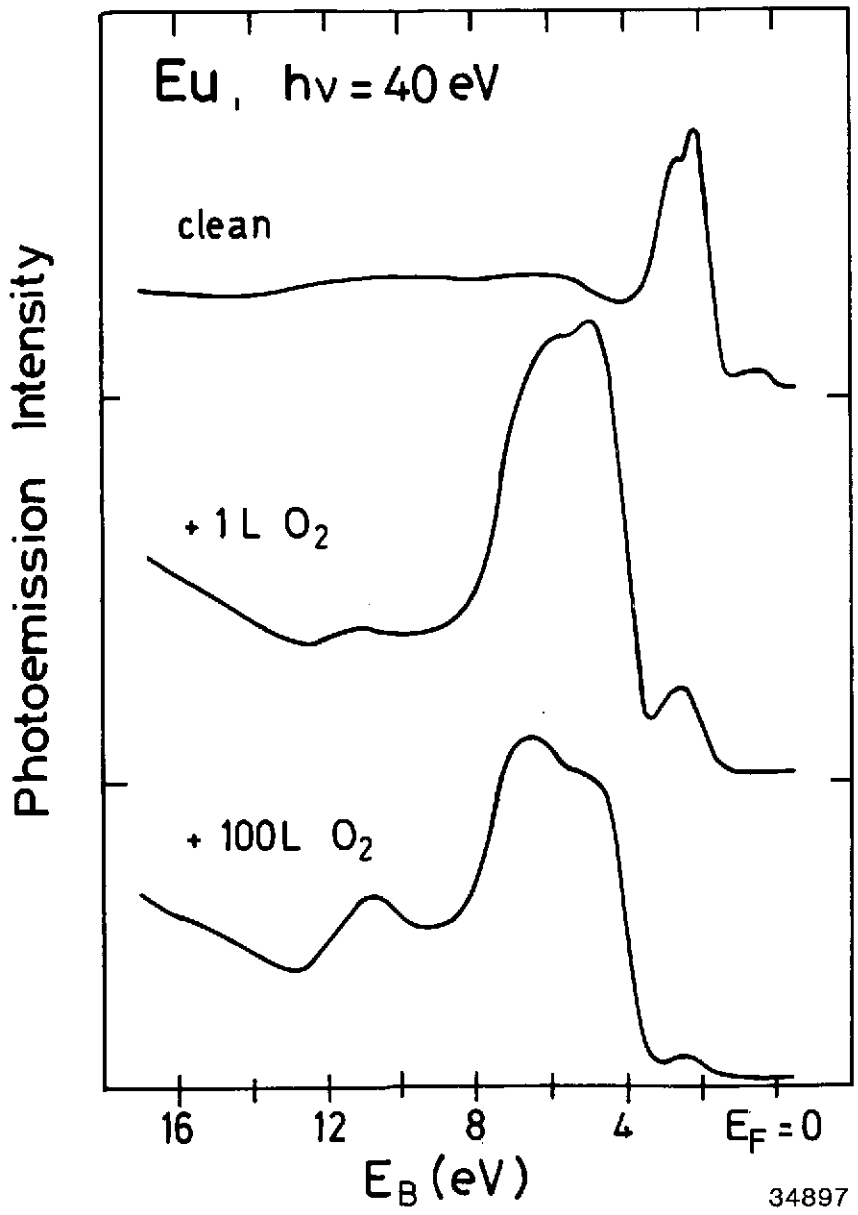

Eu, hν = 40 eV
clean
+ 1 L O_2
+ 100L O_2
Photoemission Intensity
16
12
8
4
$E_F = 0$
E_B (eV)
34897

Fig. 1

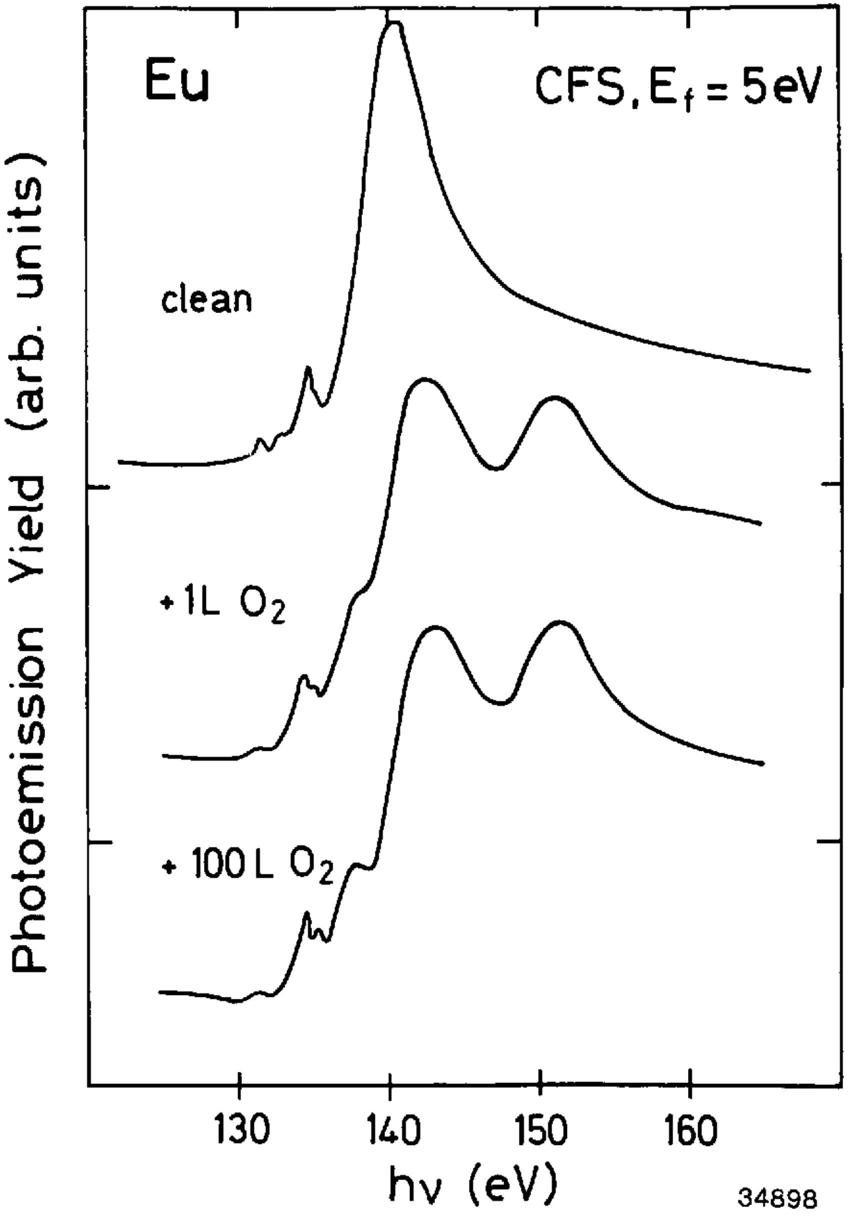

Eu
CFS, $E_f = 5$ eV
clean
+ 1L O_2
+ 100 L O_2
Photoemission Yield (arb. units)
130
140
150
160
hν (eV)
34898

Fig. 2

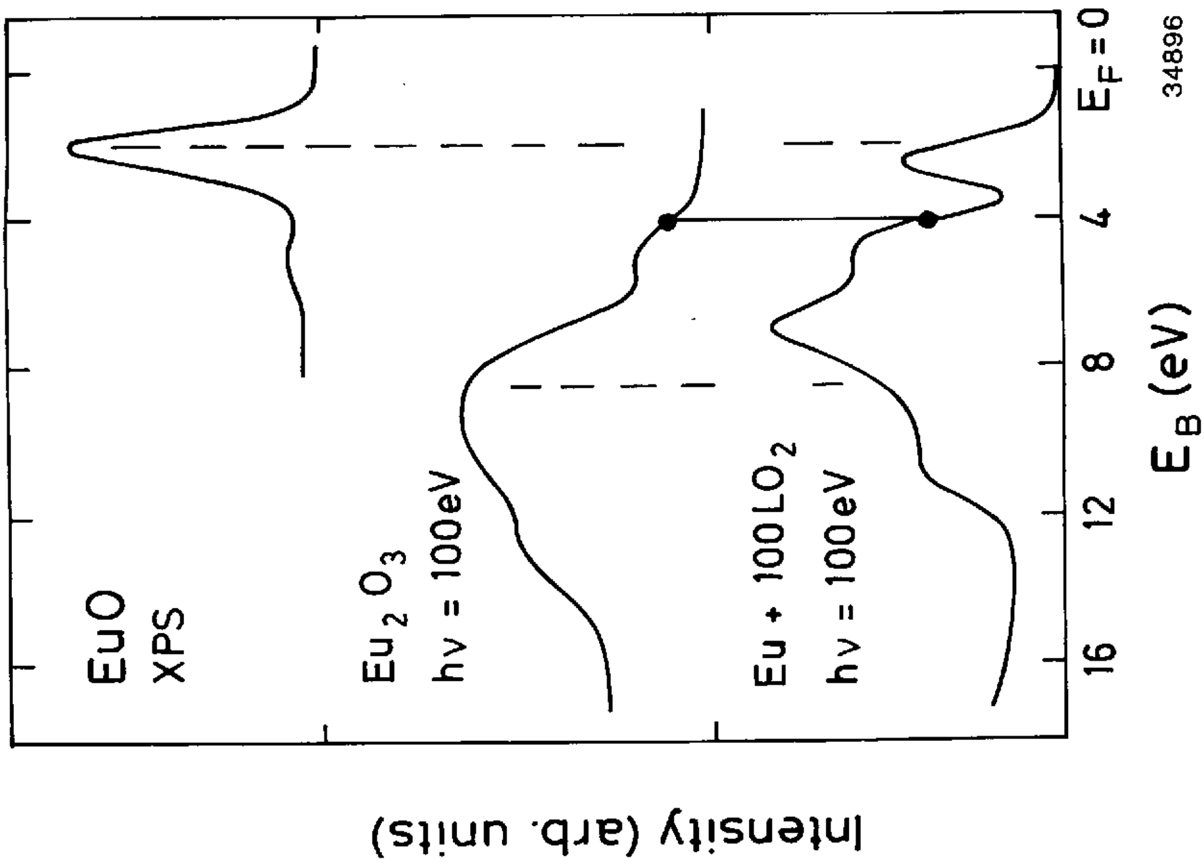

EuO
XPS
Eu$_2$O$_3$
hν = 100eV
Eu + 100LO$_2$
hν = 100eV
Intensity (arb. units)
16
12
8
4
E$_F$ = 0
E$_B$ (eV)
34896

Fig. 4

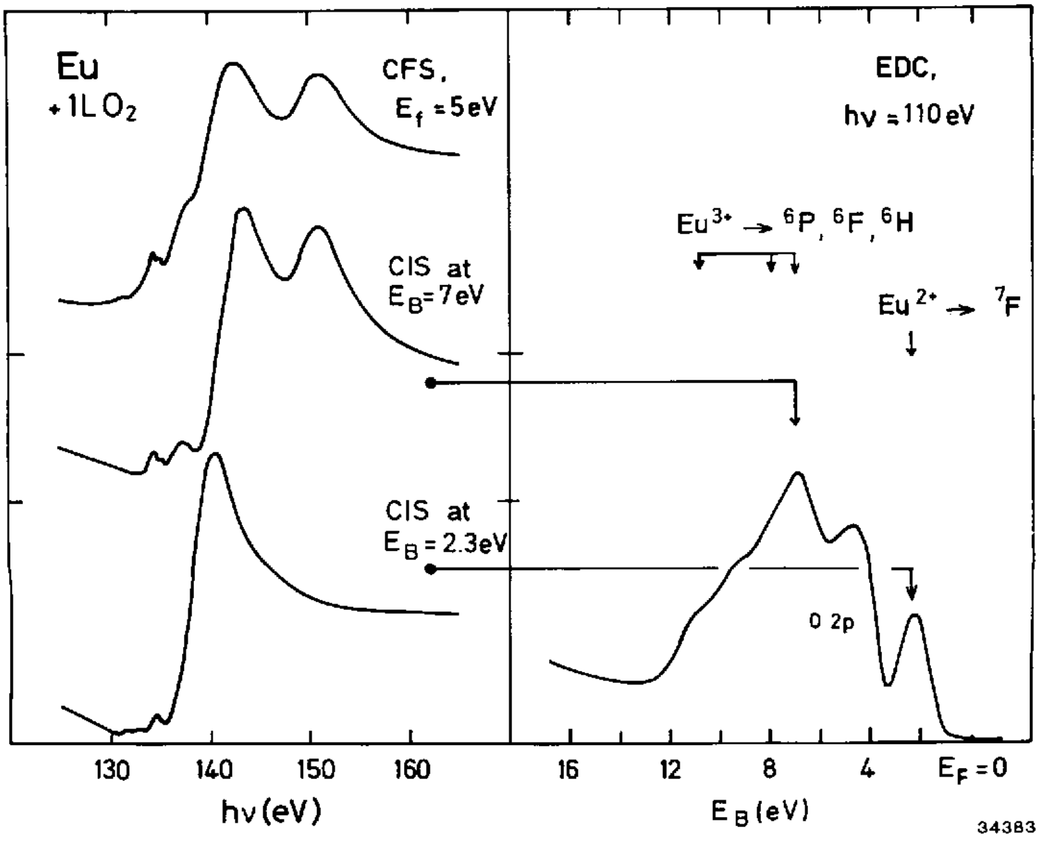
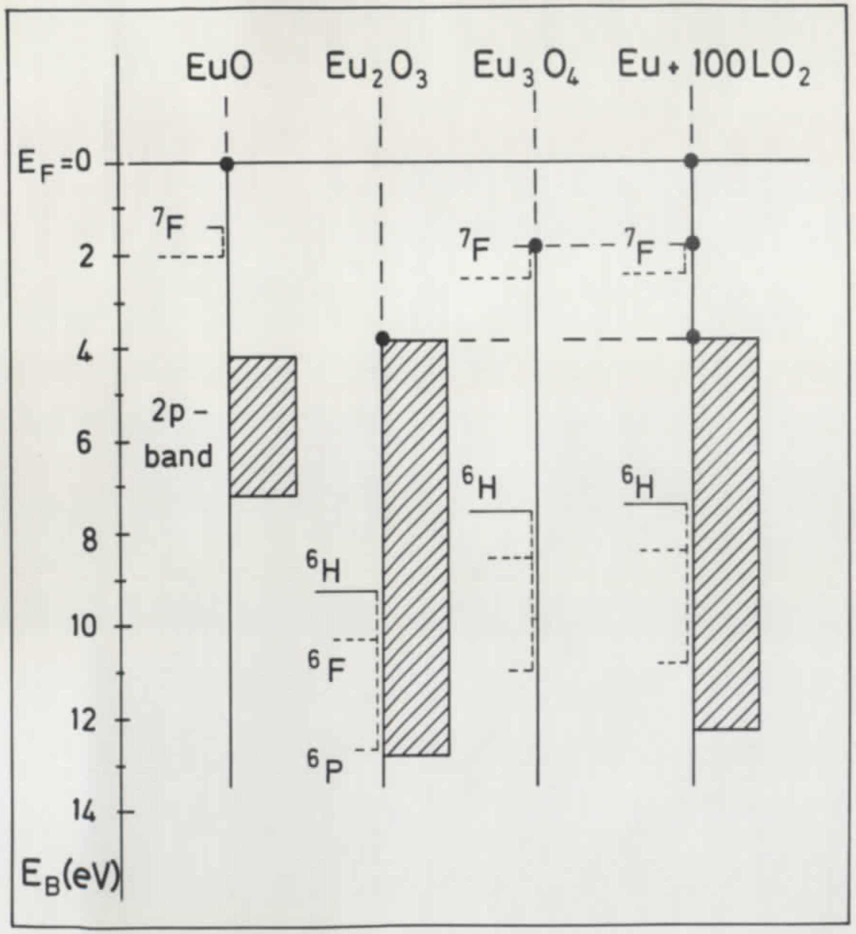

Eu
+1LO$_2$
CFS,
E$_f$ = 5eV
CIS at
E$_B$ = 7eV
CIS at
E$_B$ = 2.3eV
EDC,
hν = 110 eV
Eu^{3+} → ^{6}P, ^{6}F, ^{6}H
Eu^{2+} → ^{7}F
0 2p
130
140
150
160
hν (eV)
16
12
8
4
E$_F$ = 0
E$_B$ (eV)
34383

Fig. 3



34899

Fig. 5

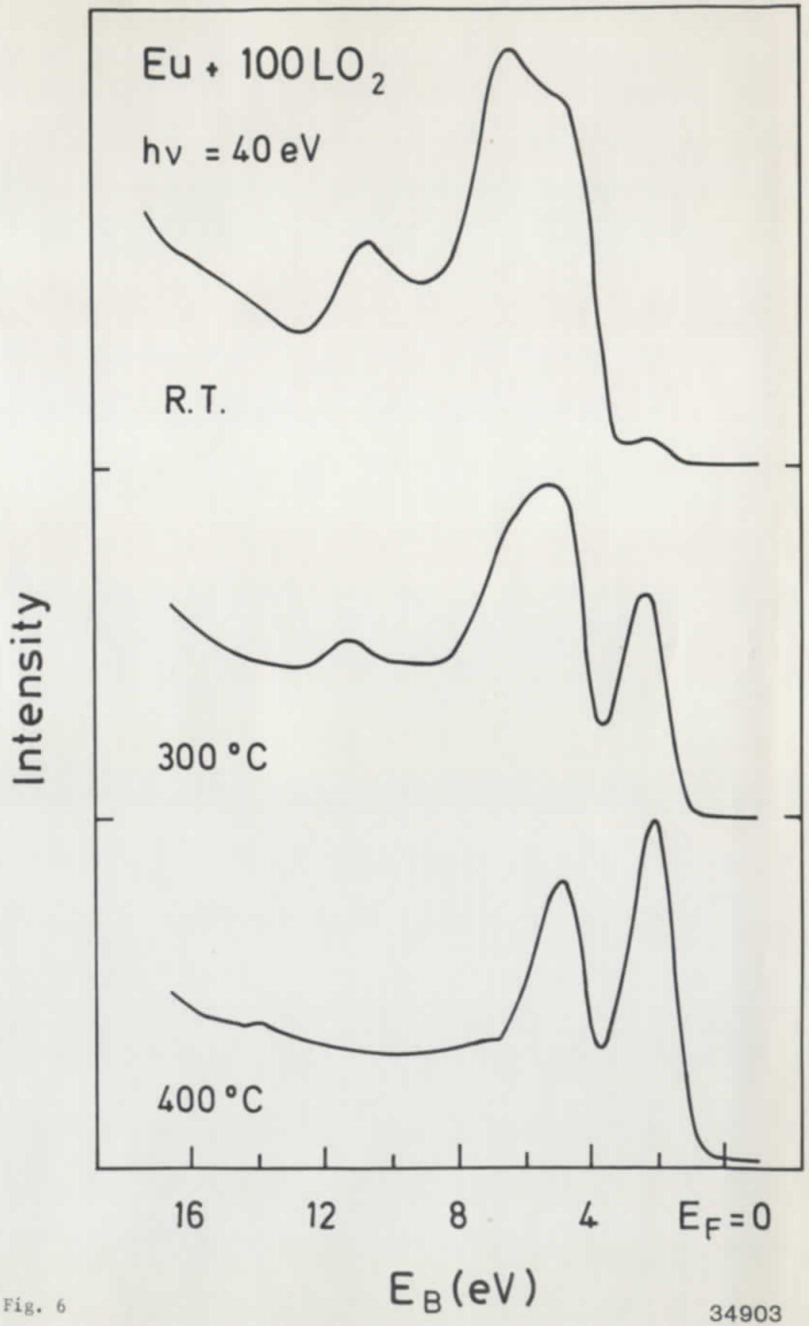


Fig. 6

34903