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J. Naegele

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APPLICATION OF ESCA AND AES TO HIGHLY RADIOACTIVE MATERIALS

J.R. Naegele

Commission of the European Communities, Joint Research Centre, Karlsruhe Establishment, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe, F.R.G.

Résumé

Description détaillée d'un spectromètre à photoélectrons et spectromètre Auger à hautes performances utilisés pour l'étude de matériaux radioactifs. Quelques résultats relatifs aux actinides métalliques et aux oxydes sont discutés.

Abstract

A commercial spectrometer for high performance photoelectron and scanning Auger electron spectroscopy on highly radioactive materials is described in detail. Some selected results for actinide metals and oxides are presented.

UPS/XPS and AES* have proven very powerful for electronic structure and chemical composition studies: The energy distribution of the emitted electrons is characteristic for each element because it is determined by the binding energy (UPS/XPS) or the energy separation (AES) of occupied electronic states. Information about the chemical bond is obtained from the energy shift (chemical shift) and shape of emission lines induced by a specific chemical environment of an atom; in addition, UPS/XPS directly examines valence and conduction electrons.

Only a few results have been published on highly radioactive actinides, mainly because of their radiation hazard. The first and pioneering XPS study for electronic structure investigation has been published on very thin actinide oxide films of low overall radioactivity. Recently, a few low resolution XPS measurements have been reported for bulk Pu²⁻⁵.

Our aim was to construct a spectrometer for XPS, AES and in particular high resolution UPS on highly radioactive bulk materials; the study of the contribution of actinide 5f electrons to the chemical bond was emphasized. Such a spectrometer needs to be protected because of the radioactive radiation. Due to the high surface sensitivity, "in-situ" sample preparation under ultrahigh vacuum ($p < 10^{-8}$ Pa) is obligatory and should not be performed in the analysis chamber to avoid a high background noise from accidental radioactive contamination of the electron energy analyzer. The mere inclusion of the complete commercial spectrometer (Leybold-Heraeus LHS-10) into a glove box system as previously described^{4,5} would have been simple but has major disadvantages, in particular for the higher surface sensitive UPS and AES:

1. Spectrometer baking temperatures higher than 100°C to achieve the obligatory UHV- conditions within reasonable time cannot be afforded because of dangerous increase of temperature of the glove box atmosphere.
2. The handling of the spectrometer is considerably impeded.
3. The original preparation chamber reaches only 10^{-7} Pa due to the O-ring sealed sample introduction system.

Therefore a quite different concept was developed as shown in Fig.1:

1. A new preparation chamber (PCh) was designed for a pressure better than 10^{-8}

*UPS/XPS: Ultraviolet or X-ray induced Photoelectron Spectroscopy; ESCA (name in the early days of photoelectron spectroscopy): Electron Spectroscopy for Chemical Analysis. AES: Auger Electron Spectroscopy.

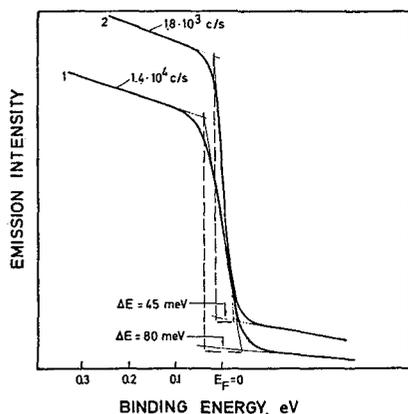


Fig. 3 Gold Fermi edge as recorded in UPS (21.2 eV excitation) at $T=80\text{K}$; electron pass energy, recording time and maximum intensity in the valence band are:

curve 1: 5eV, 10 min., 4×10^5 c/s
 curve 2: 2eV, 15 min., 5×10^4 c/s

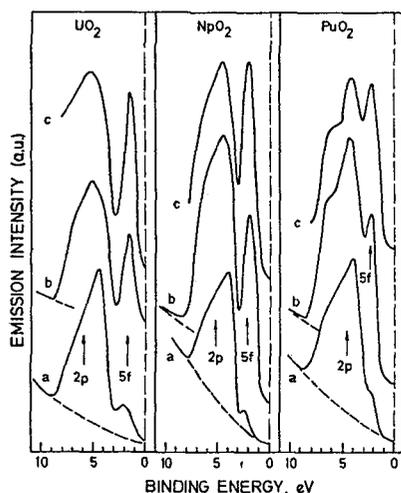


Fig. 4 UPS valence band spectra of actinide dioxides for excitation energies of 21.2 (a), 40.8 (b) and 48.4 eV (c)

The performance of the spectrometer is demonstrated in Fig. 3. High counting rates are of special importance for higher surface sensitive UPS and AES, to permit short recording times for chemically highly reactive materials without build-up of contamination on the surface. This also means that only a few cleaning cycles are necessary thus keeping low the level of radioactivity in the vacuum chambers. For XPS the gold 4f doublet is typically recorded within 10 minutes (1.5×10^7 c/s, resolution of 1.0 eV at FWHM and a pass energy of 20 eV). XPS/UPS investigates large areas of about 20 mm^2 and can therefore be regarded as a microanalytic technique only from the viewpoint of volume (about $(25 \mu\text{m})^3$). Real microanalysis is performed by AES because of the small spot of the rasterable electron gun (diameter down to $3 \mu\text{m}$).

Some selected UPS/XPS studies will be presented in the following but no AES study since the electron gun was delivered only recently.

Fig. 4 shows valence band spectra of some actinide oxides⁶ for which the actinide 5f electrons are localized. The oxygen 2p and actinide 5f levels have been clearly identified by their specific excitation probability dependent on the photon energy; the expected 5f final state multiplet components previously calculated and claimed to have been observed are not present because of strong phonon broadening.

Fig. 5 shows the first direct experimental confirmation that Am is the first rare earth like metal in the actinide series whereas the actinides up to Pu metal are transition metal like^{7,8}: The f states in Am and Sm are localized and show the expected final state multiplet splitting whereas the 5f states of Pu are delocalized and form conduction electron states at E_F .

A different U/Pu surface composition of mixed $(\text{U/Pu})\text{O}_x$ pellets and their dissolution residues, both mounted in In, has been determined from the 4f core level spectra (Fig. 6) showing that the surface of the dissolution residue is enriched in Pu by about 8% compared to the original pellet.

The valence of Pu in HfO_2 has also been determined by XPS¹⁰. The Pu 4f core levels show clearly shake-up satellites at about 7 eV higher binding energy (see also Fig. 6) typical for the tetravalent oxidation state.

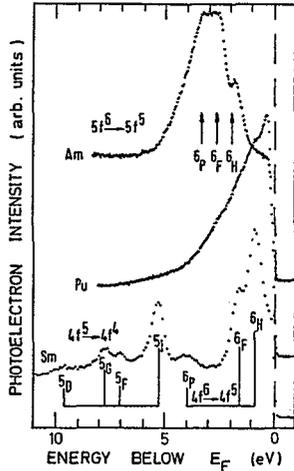
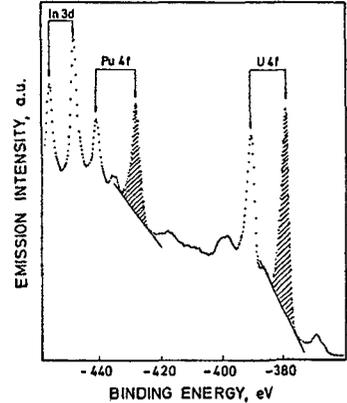


Fig. 5. Conduction band spectra of Am and Pu for He II excitation (40.8 eV)

Fig. 6. XPS core level spectrum of $(U,Pu)O_2$ dissolution residue.



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