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Determination of the clean 4*f* peak shape in XPS for plutonium metal

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ABSTRACT

Many of the interesting properties observed with plutonium are ascribed to the influence of 5*f* electrons, and to the degree of localisation observed within these electrons. Indeed, changes in 5*f* localisation are sensitively reflected in the final states observed in core-level photoemission measurements. However, when analysing the 4*f* manifold of elemental plutonium, it is essential to obtain spectra without the influence of oxidation, which can easily be misinterpreted as 5*f* localisation. The ideal method to extract elemental plutonium 4*f* spectra is to remove any influence of oxidation from the 'clean' plutonium data by careful measurement of the oxygen 1*s* region, and the subsequent subtraction of the unwanted oxide features. However, in order to achieve this objective it is essential to determine the relative sensitivity factor (RSF) for plutonium 4*f* and the precise shape of the 4*f* features from plutonium sesqui-oxide. In this paper, we report an experimental determination of the RSF for the plutonium 4*f* manifold using experimental data captured from two different Vacuum Generators spectrometers; an ESCALAB Mk II and an ESCALAB 220i.

1. Introduction

Many of the intriguing physical and chemical properties observed in the light actinides are ascribed to the influence and interactions of 5*f* electrons. When discussing the phenomena which induce such properties in the light actinide elements one of the most significant and widely reported is the degree of localisation demonstrated by the 5*f* electrons. For example, the early actinide elements such as uranium, neptunium and plutonium contain mainly itinerant (de-localised) 5*f* electrons and tend to adopt low symmetry structures, whereas beyond plutonium in the actinide series, where the 5*f* electrons become more localised, a tendency exists for higher symmetry structures [1]. Many authors have examined the degree of 5*f* electron localisation through photoemission experiments on actinide elements, whether indirectly through examination of 4*f* core electron states [2–9], or directly through measurement of the 5*f* valence electron states [2,6–11]. Of course, for direct measurements of the 5*f* photoelectron spectra one can simply look for evidence of the 5*f* manifold being pulled away from the Fermi level and the appearance of atomic-like spectral features to indicate localised electrons. The converse situation, where 5*f* electrons are observed at the Fermi level is indicative of itinerant electron character. However, to assess the localisation of the 5*f* electrons indirectly, by examining the core 4*f* electrons, one must look for evidence of well-screened versus poorly-screened core states occurring during the photoemission process [12]. The presence of well-screened 4*f* states implies itinerant 5*f* character, whereas poorly-screened 4*f* states imply localised 5*f* character. For example, if one recalls the photoemission spectra of americium [9] the 5*f* states are pulled back from the Fermi level by 2.8 eV and demonstrate discrete atomic-like features indicating localised character, while the 4*f* states exhibit a small magnitude, low binding energy doublet and a large magnitude, higher binding energy doublet. The 4*f* spectra of elemental americium are interpreted with the large magnitude doublet arising from the poorly-screened (6*d*7*s*) states and the small magnitude doublet arising from the well-screened (5*f*) states, suggesting localised 5*f* states which are retracted from the Fermi level.

Unfortunately, when one applies the same considerations to photoemission data from elemental plutonium [2–8,10,11] the results are not so conclusive. The 5*f* spectra exhibit a broad triangular feature with maximum intensity at the Fermi level for both pure (α) plutonium and gallium stabilised (δ) plutonium, implying mainly itinerant 5*f* character. Several authors [6–8,10,11] discuss the fact that for δ-plutonium there appear to be small structured features occurring between 0.5 eV and 1.6 eV in binding energy which could infer partially localised 5*f* states. However, all available sources demonstrate a general shape for the valance band which looks similar in both α- and δ-plutonium, implying that any change in 5*f* localisation between α- and δ-plutonium can only be small. This observation is further supported by electron energy loss spectra, which show a similar degree of 5*f* localisation for both

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α- and δ-plutonium [13,14]. However, the reported 4*f* photoemission spectra reveal a different interpretation with several authors discussing considerable localisation in δ-plutonium when compared to α-plutonium; inferred by the fact that additional 4*f* features are observed on the high binding energy side of the main, well-screened 4*f* doublet. Unfortunately, although some of the earlier papers were careful to point out that slight oxidation, forming surface Pu_2O_3, can result in 4*f* states which can easily be misinterpreted as poorly-screened 4*f* features, the vast majority of papers covering this subject do not specifically demonstrate the absence of oxygen; thus caution must be applied to determination of the degree of 5*f* electron localisation from 4*f* photoemission measurements alone.

In this paper experimental data are employed to determine the relative sensitivity factor (RSF) of photoemission from plutonium 4*f* states, in order to permit almost 'clean' elemental 4*f* data to be corrected for the presence of oxide contamination. In enabling the analyst to deduce the true elemental plutonium 4*f* manifold two further requirements transpire; firstly that accurate oxygen 1*s* measurements are captured in conjunction with 4*f* data, and secondly that the true plutonium 4*f* spectra of Pu_2O_3 is known. A previous study describing the determination of the RSF for plutonium 4*f* states exists, although this was not through experimental measurement, but via extrapolation of the early actinide RSF for uranium to provide RSF values for neptunium, plutonium, americium and curium [15].

2. Experimental

In this study two different X-ray photoelectron spectrometers were employed to determine the RSF of plutonium 4*f* states. The first, referred to as instrument A, is a Vacuum Generators ESCALAB MkII instrument using non-monochromatic Mg Kα (1253.6 eV) X-rays, the second, referred to as instrument B, is a Vacuum Generators ESCALAB 220i instrument using monochromatic Al Kα (1486.6 eV) X-rays. The polycrystalline plutonium samples employed in both instruments were sputter cleaned using Ar ions to remove gross surface contamination prior to all measurements, although in many cases oxide films were grown through controlled oxygen exposures to enable RSF determination. The derivation of the plutonium 4*f* RSF was undertaken using several samples, some of which were delta stabilised with low concentrations of gallium, whilst others were electro-refined pure α-plutonium. All spectra were corrected for the transmission function of the electron analyser in order to generate RSF values which are independent of local instrumental effects. For instrument A, the transmission function was determined using the methodology of Seah and Smith [16], whereas for instrument B the transmission function described by Hesse et al. [17] was employed, since this latter methodology specifically relates to a Vacuum Generators ESCALAB 220i spectrometer.

In this paper, the RSF of the plutonium 4*f* manifold is determined by comparison to oxygen 1*s* states for plutonium–oxygen phases of known composition. The data sets employed for RSF determination using instrument A were extensive, and thus data which consisted of anything other than oxygen and plutonium features were disregarded. Furthermore, data were also rejected if the oxygen 1*s* features did not consist of a single line arising from oxygen within the plutonium oxide lattice. Unfortunately, the data sets available for instrument B were not extensive, and so although care was taken to ensure that no species other than oxygen or plutonium were present, some evidence for higher binding energy oxygen 1*s* features was observed; although this was accounted for in the determination of the plutonium 4*f* RSF. All data assessment was undertaken using CasaXPS® [18] employing a background subtraction method described by Shirley [19].

3. Results and discussion

Under ultra high vacuum conditions the stable oxide of plutonium is Pu_2O_3, and data were initially examined from both instruments looking for the distinctive plutonium 4*f* features associated with Pu_2O_3; being a $4f_{7/2}$ peak at 424.5 eV and $4f_{5/2}$ peak at 437.2 eV [20]. Through measurement of the relative peak areas of oxygen 1*s* and plutonium 4*f* states from data which appear to be Pu_2O_3 one can approximate the RSF for plutonium 4*f*. This crude RSF was then employed to derive approximate 4*f* peak shapes for pure PuO_2 and elemental plutonium. A more precise determination of the RSF was then attempted, employing spectra in which the extent of oxidation is not strictly defined by stoichiometry, as in the initial Pu_2O_3 approximation, but is obtained by fitting using the peak shapes obtained for Pu_2O_3, PuO_2 and elemental plutonium. By plotting the plutonium 4*f* to oxygen 1*s* ratio as a function of the Pu_2O_3 purity of the sample under examination (shown as the extent of non-Pu_2O_3 in Figs. 1 and 2), one can determine the RSF with increased accuracy. In other words, rather than simply taking the value of the RSF from the few data which were near to perfect Pu_2O_3 stoichiometry, we have used a far wider data set and extrap-

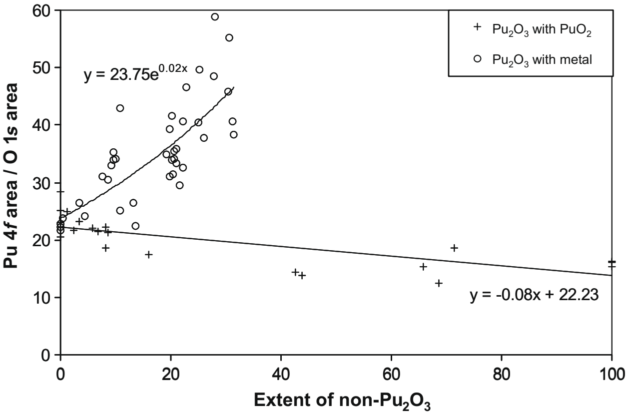

Fig. 1. Extrapolation of the plutonium 4*f*: oxygen 1*s* ratio to Pu_2O_3 for instrument A (Mg excitation), with the open circles showing data with oxidation less than Pu_2O_3 and the crosses showing data with oxidation greater than Pu_2O_3. A ratio of 23.0 ± 1.0 is determined for pure Pu_2O_3, leading to a RSF of 98.3 ± 4.3 for plutonium 4*f* when referenced against an RSF for carbon 1*s* of 1.

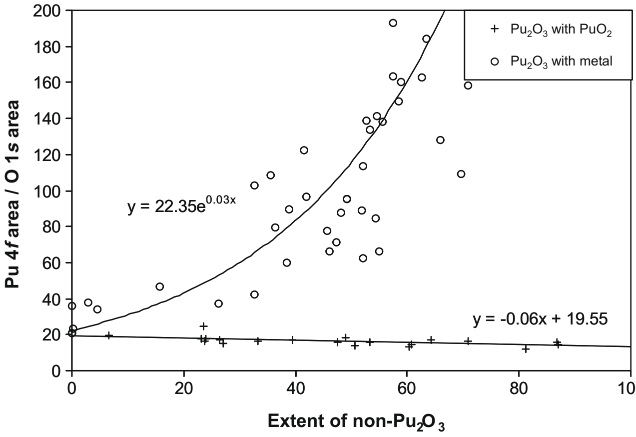

Fig. 2. Extrapolation of the plutonium 4*f*: oxygen 1*s* ratio to Pu_2O_3 for instrument B (Al excitation), with the open circles showing data with oxidation less than Pu_2O_3 and the crosses showing data with oxidation greater than Pu_2O_3. A ratio of 20.9 ± 1.7 is determined for pure Pu_2O_3, leading to a RSF of 92.1 ± 7.5 for plutonium 4*f* when referenced against an RSF for carbon 1*s* of 1.

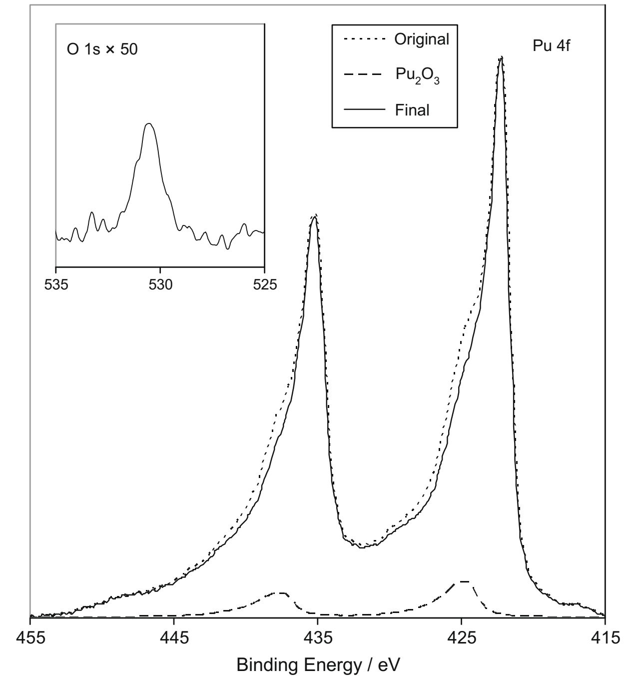

Fig. 3. A background subtracted plutonium 4*f* spectrum from electro-refined α-plutonium acquired using instrument A (Mg excitation), with the original data shown as dots, the quantity of Pu_2O_3 to be subtracted shown as dashes, and the resultant elemental plutonium signal shown as a solid line. The insert shows the oxygen 1*s* region magnified by 50 times.

olated to pure Pu_2O_3 stoichiometry using a linear function where the plutonium 4*f* features were oxidised beyond Pu_2O_3, and using an exponential function where the 4*f* features were less oxidised than Pu_2O_3. Obviously, it is still necessary to make the assumption that for Pu_2O_3 (i.e. extent of non-Pu_2O_3 = 0%) the oxygen to plutonium ratio is exactly 1.5.

Figs. 1 and 2 show the extrapolation of relative area data to pure Pu_2O_3 for both instruments A and B, respectively, and allow for an estimate of the experimental uncertainty. For instrument A (Mg excitation) the area ratio was determined to be 23.0 ± 1.0 for pure Pu_2O_3, which relates to an RSF for plutonium 4*f* of 98.3 ± 4.3, when referenced against carbon 1*s* (i.e. RSF for C 1*s* = 1). For instrument B (Al excitation) the area ratio was determined to be 20.9 ± 1.7 for pure Pu_2O_3, which relates to an RSF for plutonium 4*f* of 92.1 ± 7.5, again referenced against carbon 1*s*. For photoemission measurements the RSF value for a particular transition varies depending on the excitation energy employed; usually the Kα lines of either Mg or Al. If one considers the relationship between RSF values which relate to Mg excitation and those which relate to Al excitation for the 4*f* states of the early actinides, one should expect to find for plutonium that the RSF measured using Mg Kα is 4.4% smaller than the RSF measured using Al Kα [21]. The values reported here for the RSF of plutonium 4*f* electronic states are consistent with this theoretical 4.4% reduction between the RSF using Al excitation and that using Mg excitation if one accounts for the reported uncertainties in our measured values. To compare the RSFs obtained here to the extrapolated data of Gouder et al. [15], who obtains a value of 10.21 for the RSF of plutonium $4f_{7/2}$ when referenced against fluorine 1*s*, we must scale the RSF for the full 4*f* manifold and for reference against carbon 1*s*. If this is done one obtains a value of 76 for the RSF of the plutonium 4*f* manifold from Gouder et al. [15]. Thus, the experimentally determined RSF values obtained here are larger than the extrapolated prediction made by Gouder et al. [15] by around 25%.

Now that RSFs for plutonium 4*f* states have been determined, this information can be used to correct ‘clean’ elemental plutonium data for any slight surface oxidation. Fig. 3 shows data collected using instrument A from an electro-refined pure α-plutonium sample. Both the oxygen 1*s* and plutonium 4*f* regions were collected simultaneously, with the oxygen 1*s* data being employed in conjunction with the RSF derived above to correct the data, and remove the influence of oxidation. The insert in Fig. 3 shows a small oxygen feature, which corresponds to the Pu_2O_3 peaks shown as dashes at the bottom of the main figure. The dotted line shows the original plutonium 4*f* manifold prior to subtraction of the Pu_2O_3 peaks, while the solid line in the figure represents the true elemental α-plutonium spectra obtained. Prior to Pu_2O_3 subtraction it is tempting to ascribe the shoulders on the high binding energy side of the main itinerant 4*f* doublet as localised features. However, after subtraction of the Pu_2O_3 features we see the true nature of the 4*f* spectra, which is almost entirely itinerant in character.

4. Conclusions

We have experimentally determined the RSF for the plutonium 4*f* manifold using two different spectrometers, and using both magnesium and aluminium excitation sources. The values obtained for the RSF, referenced to carbon 1*s*, for plutonium 4*f* states are 98.3 ± 4.3 and 92.1 ± 7.5 for excitation using Mg Kα and Al Kα, respectively. The use of the determined RSF to obtain clean elemental plutonium 4*f* spectra has been demonstrated on electro-refined α-plutonium, and the influence of not applying such corrections has been discussed.

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