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TEM-EELS analyses of protactinium

O Dieste, TWiss, J-C Griveau, R J M Konings, G van der Laan and R Caciuffo

1 European Commission, Joint Research Centre (JRC), Directorate for Nuclear Safety and Security, Postfach 2340, D-76125 Karlsruhe, Germany
2 Magnetic Spectroscopy Group, Diamond Light Source, Didcot, OX11 0DE, United Kingdom
E-mail: oliver.dieste-blanco@ec.europa.eu

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Abstract

A fragment of metallic protactinium (Pa) has been studied using a transmission electron microscope (TEM) equipped with an electron energy loss spectroscopy (EELS) detector. Bright and dark field TEM images have been acquired, and selective area electron diffraction (SAED) has been used to study the crystal structures. The results showed the presence of domains both of metallic and of oxidized material that likely occurred during sample preparation. EELS edges have been collected for the first time for the oxide compounds and compared with those computed using many-electron atomic spectral methods.

Introduction

Discovered in 1917, protactinium is one of the rarest naturally occurring elements, and the longest-lived $^{231}\text{Pa}$ isotope is present in natural samples only in very low concentrations [1]. It is, formally, the third element of the actinide series and the first having 5f electrons [2]. Among the light actinides, protactinium is one of the least studied elements, partially due to the limited availability of material and the absence of technological applications, but also because of its high gamma activity and radiotoxicity [2, 3]. As a result, most of the experimental studies have been performed on small quantities of material, and not so much on bulk samples. For the same reasons, electron microscopy studies of protactinium and its compounds are rare. As only technology relevant aspect where protactinium presence is relevant nowadays one could think on the Molten Salt Reactors (MSR) where the production of $^{233}\text{Pa}$ from neutron capture could be of concern (inhibition of $^{233}\text{U}$ production) so to require separation of such a waste species. Therefore a good knowledge of the protactinium chemistry (hence knowing its electronic properties) could be of significant importance [4].

Among the techniques which are available nowadays in a transmission electron microscope (TEM), electron energy-loss spectroscopy (EELS) gives information on the elemental composition of a sample, with nanometric spatial resolution and high energy resolution ($\sim 0.6$ eV) [5]. The measured spectra give the same information as obtained from x-ray absorption near edge structure (XANES) technique, but with some advantages: i) EELS does not require the use of a synchrotron facility, which makes the measurement procedure easier and faster; ii) the spatial resolution allows one to perform EELS on different regions of the sample; the technique is thus local and not global (as in the case of XANES); iii) EELS is a non-destructive technique, which permits to continue studying the sample after the analysis and complement it with other techniques, for instance imaging and elemental analyses by energy-dispersive x-ray (EDX) spectroscopy. The principal drawback is that the energy resolution is lower than that of the XANES technique, making the study of the drifts or changes in the spectra more complex.

In this paper we report a detailed TEM study of protactinium metal from an archive sample. We studied the microstructure of the aged material ($\sim 40$ years old) and collected EELS edges, which are compared with the results of multielectron atomic spectral calculations with interaction parameters obtained by using the Hartree–Fock (HF) scheme of Cowan [6] in intermediate coupling approximation.
Experimental

The protactinium metal (electronic structure [Rn]5f$^2$6d$^2$7s$^2$) batch used in this study was produced by a Van Arkel technique in the late 1970s [7–9]. Pellets of the oxide phase of $^{231}$Pa (Pa$_2$O$_5$) mixed with graphite powder underwent a carbo-reduction in a radio-frequency heated crucible at 2273 K under high vacuum to produce PaC. The resulting material and iodine were sealed under high vacuum in a quartz ampoule and heated up to 823 K. Protactinium metal deposited on a heated tungsten sphere at 1473 K was separated subsequently by levitation melting in a Hukin crucible. The initial composition analysis of the resulting metal indicated a high purity Pa metal (530 and 1420 atom ppm of non-metallic and metallic impurities, respectively) at the production time (1978). Several measurements have been performed on this high-purity sample, such as transport properties [11], heat capacity [12], magnetic susceptibility [7], and crystallographic structure under pressure [13]. Low temperature $\alpha$ magnetic susceptibility measurements clearly demonstrated that Pa metal is the first 5f element in the actinides series to be superconducting at 0.43 K [14].

Due to the high alpha self-irradiation taking place in the sample ($T_{1/2} = 3.276 \times 10^4$ yr), it is important to determine the impact of defects and decay daughters accumulated since the purification process. We performed a decay simulation by the Nucleonics software [15] (considering a 40 years period since the synthesis) and experimental magnetic measurements by a Quantum Design MPMS-7T superconducting quantum interference device on a piece of the thermally refreshed batch used for this study. An estimation of the impurities amount produced by self-decay during this period suggests a slight increase, below 0.1% at, of the stable $^{207}$Pb and of the long-living $^{227}$Ac isotopes (see table 1). Magnetic susceptibility measurements at 7 T of the refreshed sample shows a temperature independent behavior from room temperature down to 2 K, as previously reported for the initially produced Pa metal [9].

The study presented here was performed on a FEI’s Tecnai$^\text{TM}$ G2 TEM, equipped with an EDAX energy dispersive x-ray detector and a GATAN Tridiem camera with imaging filter. EELS was performed with apertures between 1 and 5 mm, energy dispersion between 0.2 and 0.5 eV/channel, and focal distance between 34 and 192 mm, taking care to have, at each energy value, a collection angle larger than the dispersion one. The field emission gun was operated at 200 kV. The TEM has been adapted for the examination of highly active or irradiated nuclear materials thanks to a flange that has been inserted in the octagon hosting the objective lenses, and a glove box mounted on this flange around the compustage [16]. Thus, the sample can be transferred from the glove box where it is prepared to the microscope making use of a La Calhène DPTE® system. Due to the small amount of material (the original sample was 43 $\mu$g in weight), the sample was prepared by the crushing method [17]; the small grain was crushed in an agate mortar similarly to a ceramic sample, obtaining only extremely small particles detached from the initial one mixed with large amount of dust and other contaminants coming from the used tools and resin used for embedding it (carbon, silicon, magnesium, iron, chrome and calcium among others). Finally a suspension of the obtained powder in methanol was dropped on standard copper grids coated with carbon film (Formvar). These grids were introduced in a plasma cleaner in order to eliminate any organic residues, and further introduced in the transmission microscope for the analyses.

| Nuclides | Half-life | Decay modes | at % | $\alpha$ particles ($\times 10^{15}$) |
|----------|-----------|-------------|------|----------------------------------|
| $^{231}$Pa | 32.76 ky | $\alpha$; $^{24}$Ne; SE; $^{25}$F | 99.8 | 2200 |
| $^{227}$Ac | 21.773 y | $\beta$; $\alpha$ | 0.048 | 13.2 |
| $^{227}$Th | 18.718 d | $\alpha$ | $1.11 \times 10^{-4}$ | 941 |
| $^{228}$Ra | 11.43 d | $\alpha$; $^{16}$C | $6.85 \times 10^{-5}$ | 952 |
| $^{228}$Rn | 3.96 s | $\alpha$ | $2.75 \times 10^{-10}$ | 952 |
| $^{210}$Po | 1.78 ms | $\alpha$; $\beta$ | $1.24 \times 10^{-13}$ | 952 |
| $^{211}$Pb | 36.1 m | $\beta$ | $1.50 \times 10^{-7}$ | 0 |
| $^{210}$Bi | 2.17 m | $\alpha$; $\beta$ | $9.04 \times 10^{-9}$ | 950 |
| $^{206}$Tl | 4.77 m | $\beta$ | $1.98 \times 10^{-8}$ | 0 |
| $^{207}$Pb | Stable | $\alpha$ | 0.036 5 | 0 |
| $^{211}$Po | 516 ms | $\alpha$ | $6.94 \times 10^{-14}$ | 2.56 |
| $^{232}$Fr | 19.8 m | $\alpha$ | $1.25 \times 10^{-9}$ | 0.00 792 |
| $^{4}$He | Stable | | 0.27 | 0 |

Total: 15 | 100 | 6970 |
Results

TEM analysis
All in all, only some sub-micrometre sized grains could be found, enough for the objectives of the present work. Many more particles were spotted, also belonging to the sample, but due to their intricate distribution within the studied material it was not possible to confirm precisely their composition, nor to obtain good images so that they were disregarded. Figure 1 shows a bright field image of one of the observed protactinium particles. The size is about 500 nm and the morphology is irregular. All the tiny objects surrounding the particle are contamination due to the crushing method already described. Bright and dark field images from the center of the particle are shown in figure 2. These images reveal the polycrystalline nature of the studied grain: small particles can be observed in dark field mode all around the grain (bright spots), which indicates they present a different orientation of those that do not appear bright.

Given the radioactivity and age of the sample, we performed an assessment of its evolution in terms of composition and potential microstructure modification due to radiation damage. An estimation of the cumulated alpha-dose has been made using the decay engine of Nucleonica [15]. An age of 40 years was accounted for, leading to the formation of $7 \times 10^{18} \alpha$ g$^{-1}$, corresponding to about 0.2 at% of helium generated as indicated in table 1. The total number of displacements per atom (dpa) in the $^{231}$Pa sample has been calculated by using the Monte-Carlo software SRIM [18], leading to a value as high as 6.35 dpa. However, since recombination can occur, the displacements calculated from the SRIM software for one alpha-decay event do not reflect the final status. Substantial amount of alpha-damage and of radiogenic helium was expected to

![](image1.png)

Figure 1. (a) TEM bright field image showing an overview of a typical grain (dark feature in the center of the image) within the sample; (b) a higher magnification view of the same particle.

![](image2.png)

Figure 2. Bright (a) and dark (b) field images of a typical grain of the sample shown in figure 1.
modify the microstructure of the sample. Moreover, as mentioned earlier, $^{227}$Ac and $^{207}$Pb have formed significantly due to the radioactive decay since the preparation date. Their presence can also have contributed in changing the sample microstructure, considering that their atomic radii are larger that the one of protactinium for in both the metallic and the oxide phases.

It is interesting to observe that other sample particles, such as the one shown in figure 3, present a monocristalline structure together with numerous particles with different orientation. Electron diffraction shows that the large particle fits with a bct structure with lattice parameters $a = 0.393 \text{ nm}$ and $c = 0.324 \text{ nm}$ (as reported for metallic protactinium in literature [19]) and is oriented along the [111] axis. Although the presence of particles other than the larger crystal cannot be easily directly observed in the image diffraction rings present in the electron diffraction image indicate the presence of a second phase in the form of small particles with different orientations. Between the pentoxide and the dioxide several intermediate compounds have been described by Roberts and Walter [20]. These compounds belong to different space groups: $\text{PaO}_2$ (fcc, $a = 5.509 \text{ nm}$), $\text{PaO}_{2.18}$–$\text{PaO}_{2.21}$ (fcc, $a = 5.473 \text{ nm}$), $\text{PaO}_{2.33}$ (tetragonal, $a = 5.425 \text{ nm}$, $c = 5.568 \text{ nm}$), $\text{PaO}_{2.40}$–$\text{PaO}_{2.42}$ (tetragonal, $a = 5.480 \text{ nm}$ $c = 5.416 \text{ nm}$), $\text{PaO}_{2.42}$–$\text{PaO}_{2.44}$ (rhombohedral, $a = 5.449 \text{ nm}$, $\alpha = 89.65^\circ$), $\text{Pa}_2\text{O}_5$ (fcc, $a = 5.446 \text{ nm}$), $\text{PaO}$ (fcc). The observed Debye–Scherrer rings do not match with the structure of any of these compounds, nor with other protactinium oxides; we hypothesize that these rings are due to the contamination of the sample, as mentioned earlier. On the slightly underfocused image of figure 3(a), the white tiny spots could be attributed to helium bubbles formed during the storage.

The third particle studied (shown in figure 4) is made up of randomly oriented nanocrystals, visible as spots of different grey level, or of different brightness in the dark field image. This polycristalline nature (the lattice misorientation between nanoparticles is recognizable as moiré fringes on the bright field image in figure 5(a)) is evidenced in its electron diffraction shown in figure 5(b). This diffraction matches with the expected fcc structure for the protactinium dioxide. Thus it is clear that the sampled metallic material has been oxidized during the sample preparation or eventually its storage, and thus oxidized, polygonised regions are found together with metallic particles.

It is important to remark here that the resolution of our system is not sufficient to calculate precisely the lattice parameter, but only to assure that the diffraction is compatible with the value found in the literature [21]. However, an estimate of the lattice parameter has been compared with a possible metallic fcc structure (formed at high temperature) and with the dioxide and pentaoxide forms None of them was matching the calculated value.

**EDS and EELS analysis**

To confirm that the particles that we are observing are part of the protactinium sample, and due to the intricate arrangement of the particles within the sample (i.e. mixed with particles coming from the metallic tools and from the agate mortar used for the sampling), we performed Energy Dispersive Spectroscopy (EDS). Figure 6 shows a typical measured spectrum, featuring protactinium peaks along with copper ones, which are due to the sample grid.

EDS analyses were performed on each particle found on the sample, but not all the edges could be clearly observed on all of them; few could be collected on pure metallic regions (namely N$_{4,5}$, but to make the collection
self-consistent, all the spectra shown in this work correspond to the same particle, which turned to be partially oxidized. Technical issues limited the spatial resolution of this technique, impeding us to obtain local information, but instead an average of an area 20 nm in diameter. Figures 7 and 8 show all edges, from the very low energy P1,2,3 edges, to the highest observed one, M3. Table 2 presents the onset energies for each of them. Some of these edges are reported here for the first time. The background has been removed with a simple exponential fitting for the O4,5,N 6,7,N 4,5,M 3 edges, and the oxygen K line: in the case of the M4,5 edges the background has been removed with two-step exponential fitting (one to remove the background before M5, and a second one to remove it before M4). For the P1,2,3 edges, and following the identification of these edges made by Degueldre et al [22], we fitted the plasmon with a Gaussian lineshape, in order to be able to observe clearly the three peaks that are partially hidden. Finally, the O4 edge position has been calculated by deconvoluting the giant resonance, and thus should be taken as an approximative position.

Computational study and oxidation state

Multiplet calculations

The M4,5 (3 d → 5f), N4,5 (4 d → 5f), and O4,5 (5 d → 5f) EELS spectra were calculated by taking the electric-dipole-allowed transitions between the ground-state 5f2 and final-state nf5f3 Pa configurations. Wave functions of ground and final states were calculated in intermediate coupling approximation using the HF scheme of Cowan with relativistic corrections [23, 24]. The Slater integrals and the spin-orbit parameters are
listed in Table 3. Interatomic screening and configuration interactions were taken into account by reducing the HF values of the Slater integrals $F_{ff}^{5,5,5}$, $G_{fn}^{5,k}$ by the factor $\kappa$ given in Table 3. To fit the experimental data, the $M_{4,5}$ calculations were broadened by a Lorentzian of Half-Width at Half Maximum (HWHM) $\Gamma = 1$ eV and a Gaussian of HWHM $\sigma = 2.8$ eV. The $N_{6,7}$ calculations were broadened by $\Gamma = 1$ eV and $\sigma = 2.5$ eV. The $O_{4,5}$ calculations were broadened by a Lorentzian of $\Gamma = 1.5$ eV for the pre-peak, and a Fano line shape of $\Gamma = 3.5$ eV and $q = 2.7$ for the main peak.

$M_{4,5}$ edges
Since the electrostatic interactions (values in Table 3) are smaller than the line broadening, no clear multiplet structure is visible, but instead the calculations show two nearly symmetric peaks separated in energy by the 3d
spin-orbit splitting, given by \( \frac{5}{2} \times \zeta(3d) \) as seen in figure 9. The extra peaks are not part of the M\(_{4,5}\) edge of the metallic element, and have been attributed to electron transitions from the 5f states in the conduction band, similar to the transition to the 4f band in cerium dioxide [25].

Several spectra have been collected on different regions of the sample. Making use of the second derivative method [5] we calculated the branching ratio for each of the collected spectra, proving that the oxidation state was not equal on all of them (something already expected after the electron diffraction showing metallic and oxidized regions). The analysis of the N\(_{4,5}\) edges put some more light on this fact.

**N\(_{4,5}\) edges**

Due to the linewidth broadening (both intrinsic and extrinsic), the multiplet structure is not clearly observed in the N\(_{4,5}\) edges shown in figure 10. However, the N\(_{4,5}\) edges allows a more accurate determination of the

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**Figure 8.** EELS spectra of the protactinium: (a) oxygen K edge, (b) N\(_{4,5}\) edges, (c) M\(_{4,5}\) edges and (d) small M\(_{3}\) edge. All spectra have been normalized to the maximum value within each graph. Blue areas represent the edges after the removal of the background; their scales have been arbitrarily changed for an easier observation.

**Table 2.** EELS edges for Pa and their onset energy observed.

| Edge  | Peak | Transition | Energy (eV) |
|-------|------|------------|-------------|
| P\(_{3,2,1}\) | P\(_3\) | \(6\sigma_{3/2} \rightarrow 5\sigma_{5/2}\) | 11.6 |
| P\(_{3,2,1}\) | P\(_2\) | \(6\sigma_{3/2} \rightarrow 5\sigma_{5/2}\) | 21.3 |
| P\(_{3,2,1}\) | P\(_1\) | \(6\sigma_{3/2} \rightarrow 5\sigma_{5/2}\) | 29.3 |
| prepeak | \(\Delta\sigma(5d \rightarrow 5f)\) | | 89 |
| O\(_{4,5}\) | O\(_3\) | \(5d_{5/2} \rightarrow 5f_{5/2}\) | 95.8 |
| O\(_4\) | \(5d_{3/2} \rightarrow 5f_{5/2}\) | 102 |
| N\(_{6,7}\) | N\(_7\) | \(4f_{5/2} \rightarrow 5f_{7/2}\) | 351.5 |
| N\(_6\) | \(4f_{5/2} \rightarrow 5f_{7/2}\) | 365 |
| O K-line | O K | \(1s_{1/2} \rightarrow 2p_{1/2}\) | 526.8 |
| N\(_{4,5}\) | N\(_3\) | \(4d_{5/2} \rightarrow 5f_{5/2}\) | 705 |
| N\(_4\) | \(4d_{3/2} \rightarrow 5f_{5/2}\) | 3453 |
| M\(_{4,5}\) | M\(_3\) | \(3d_{5/2} \rightarrow 5f_{5/2}\) | 3453 |
| M\(_4\) | \(3d_{3/2} \rightarrow 5f_{5/2}\) | 3625 |
| M\(_3\) | \(3p_{3/2} \rightarrow 5f_{5/2}\) | 4186 |

* See clarifications in the text.
branching ratio compared to the M_{4,5} ones, where the spin-orbit split core levels are far apart, so that normalization errors in the experimental spectra can play a role.

The possible electronic configurations for protactinium are [Rn]5f^2 6d^1 7s^2 for metallic, [Rn]5f^2 6d^1 for monoxide (which has been reported only as a thin layer over the surface of metallic bulk material in [19]), [Rn]5f^4 for dioxide and [Rn]5f^6 for the pentoxide form, the most stable of the oxidations forms for protactinium [2]. Making use of the calculations from the literature [26, 27], we assessed the values for the branching ratio for 5f^0, 5f^1 and 5f^2 obtaining 0.591, 0.634 and 0.680, respectively. Figure 11 presents the branching ratios obtained from different locations of the sample both for the N_{4,5} and the M_{4,5} edges, and their respective calculated 5f occupancy. It can be observed that the oxidation state of the material varies between a 5f^2 state (corresponding to metallic protactinium) down to 5f^0 (corresponding to Pa_2O_5), with the majority of the investigated regions being a mixture between oxidized and metallic material.

**O_{4,5} edges**

Since the 5d core and 5f valence shells have the same principal quantum number n, i.e., have a large radial overlap, the 5d-5f electrostatic interactions are much larger than the spin-orbit interaction of the shallow 5d level. The large radial overlap also leads to a huge value for the radial-matrix element (see table 3).

The smaller prepeak that is observed in figure 12 is a consequence of first-order perturbation by the 5d spin-orbit interaction on the 5d-5f exchange splitting. Thus, the small pre-peak in the actinide 5d-5f transition should not be labelled as the O_5 peak, but rather the \( \Delta S = 1 \) peak [28]. In the absence of spin-orbit interaction the prepeak would be forbidden.

### Table 3. Core-level spin-orbit interaction \( \zeta(nd), Slater integrals (F^n, G^n)(all in eV), radial dipole matrix element (R1) and Slater reduction factor (\kappa) for the final states Pa nd5f^2.

|          | n = 3 | n = 4 | n = 5 |
|----------|-------|-------|-------|
| \( \zeta(nd) \) | 69.097 | 16.266 | 2.915 |
| \( F^2(5f, nd) \) | 2.167 | 4.376 | 9.590 |
| \( F^4(5f, nd) \) | 0.996 | 1.718 | 6.081 |
| \( G^1(5f, nd) \) | 1.675 | 0.762 | 11.094 |
| \( G^3(5f, nd) \) | 1.011 | 0.813 | 6.832 |
| \( G^5(5f, nd) \) | 0.707 | 0.685 | 4.864 |
| \( (nd||R1||5f) \) | -0.043 76 | -0.096 82 | 1.563 40 |
| \( \kappa \) | 0.8 | 0.8 | 0.67 |

Figure 9. Example of observed (open symbols) and calculated (solid line) M_{4,5} edges for the protactinium.
Figure 10. Experimental (open symbols) and calculated (solid line) $N_{4.5}$ edges for the protactinium (metallic).

Figure 11. Calculated $f$ occupancy as function of the experimental value (symbols) of branching ratio obtained from the $M_{4.5}$ and $N_{4.5}$ edges. Dotted lines indicate the nominal oxidation states for Pa dioxide and Pa metal.

Figure 12. Observed (open symbols) and calculated (solid line) $O_{4.5}$ edges for the protactinium with the expected prepeak.
For the $f^2(\alpha H\alpha)$ state, the dipole-allowed transition are to $^2G_v$, $^2H_i$, and $^1I_f$ states with $J = 3$, 4, and 5. In intermediate coupling, the ground state is a mixture of different LS states, namely 88% $^3H_4$, 1% $^3P_0$, and 11% $^1G_4$. Analysis of the prepeak structure shows that it contains a mixture of mainly triplet and quintet spin states. The main peak around 110 eV consists of mainly J = 3 and 4. The shoulder at ~99 eV consists of $J = 5$. The prepeak at ~95 eV is a mixture with $J = 5$ as the main component. Further confirmation of this assignment has been obtained by non-resonant inelastic x-ray scattering (NIXS) [29, 30].

Because at higher energies the localized 5d$^5$7f$^2$ final states have a large configuration interaction with 6d and 6f continuum states, the main peak shows a strong Fano line shape [31] (with an asymmetry parameter $q = 2.7$). While it is difficult to take these interactions with the continua properly into account, the net effect is an increase in the electronic screening, i.e., a reduction of the Slater integrals. Indeed a reduction from 80% (for M$_{4,5}$ and N$_{4,3}$) to 67% (for O$_{4,3}$) gives a good agreement with the experimental spectra, as shown in figure 12.

Conclusions

Transmission electron microscopic investigations of an aged metallic protactinium sample showed the presence of both polycrystalline metallic and oxidized regions. EELS spectra have been recorded and compared with theoretical spectra obtained by multi-electron atomic calculations. On this basis the analysis of the experimental EELS spectra of the different regions indicated a range of oxidation states, principally between the metal and the dioxide. The oxidation is likely due to have occurred during the sample preparation, which increases the surface area of the particles significantly. This can be overcome in the future by using the focused ion beam (FIB) technique for producing thin lamellae under controlled conditions, rather than the mechanical crushing method applied in this work. Such studies will shed light on the O$_{4,5}$ giant resonance, which could not be clearly deconvoluted in this work, and will allow the identification of the exact oxidation state of the material as a function of the depth in the bulk.

ORCID iDs

O Dieste https://orcid.org/0000-0002-8436-2302
R Caciuffo https://orcid.org/0000-0002-8708-6219

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