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Probing Electronic Structure in Berkelium and Californium via an Electron Microscopy Nanosampling Approach

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ABSTRACT

Due to their rarity and radioactive nature, comparatively little is known about the actinides, particularly those with atomic numbers higher than that of plutonium, and their compounds. In this work, we describe how transmission electron microscopy can provide comprehensive, safe, and cost-effective characterization using only single nanogram amounts of highly-radioactive, solid compounds. Chlorides of the rare elements berkelium and californium were dropcast and then converted *in situ* to oxides using the electron beam. The f-band occupancies were probed using electron energy loss spectroscopy and an unexpectedly weak spin-orbit-coupling was identified for berkelium. In contrast, californium follows a *jj* coupling scheme. These results have important implications for the chemistries of these elements and solidify the status of californium as a transitional element in the actinide series.

MAIN TEXT

Many radioactive materials have unique properties and many of them play central roles in applications such as nuclear power plants and cancer therapy¹⁻⁵. However, the health hazards posed by radioactive elements have always been a major hurdle to their research. As a result, comparatively little is known about them and their chemistries. Within the actinide series from actinium (Ac) to lawrencium (Lr), of which all isotopes are radioactive, the vast majority of research has been on uranium (U), thorium (Th), neptunium (Np), and plutonium (Pu). Further, of all described actinide-containing crystal structures (~7000), only about 0.5% include elements with atomic numbers greater than that of Pu⁶. This imbalance can in part be explained by the relevance of the early actinides to nuclear power plants, space exploration, and nuclear weapons programs¹⁻⁵, in part by the natural occurrence of thorium and uranium, on which much research has been focused. Another key factor are the extreme challenges introduced when working with the heavy actinides. Transplutonium elements are without exception synthetic elements and their production requires long irradiation campaigns in high neutron flux nuclear reactions, followed by arduous purification steps performed in hot cells and using remote handling techniques⁷. These processes are time-consuming, difficult and therefore inherently expensive, yet yield only minute amounts of the targeted isotopes. The current global production capabilities are milligram amounts of berkelium-249 (²⁴⁹Bk) and californium-249 (²⁴⁹Cf), sub-microgram amounts of einsteinium-254 (²⁵⁴Es), and picogram-scale quantities of fermium-257 (²⁵⁷Fm)⁷. Furthermore, all transcurium elements except for Cf (²⁴⁹Cf, half-life ≈ 351 years) that are currently available in appreciable quantities only have relatively short-lived isotopes, which rapidly decay and emit large amounts of radiation. This prevents stockpiling and increases the logistical burden even further. Considerable efforts have therefore gone into minimizing the amounts required for experiments^{8,9}, but typical characterization techniques, such as X-ray diffraction and X-ray absorption spectroscopy still require microgram to milligram amounts per sample^{10,11}. In the case of transplutonium elements, even such small amounts can be cost-prohibitive, pose significant health hazards and necessitate large administrative and experimental controls. Only a few institutions worldwide are set up to tackle these challenging requirements, and even then, experiments can still fail due to self-irradiation-induced artifacts¹²⁻¹⁴.

In light of these challenges, the use of transmission electron microscopy (TEM), a technique allowing detection and investigation of even single atoms, seems like a promising approach¹⁵⁻²⁰. Yet, we are only aware of two research groups that have used TEM to study transplutonium elements. In the 1970's, a group at the Oak Ridge National Laboratory used TEM to solve crystal structures from polycrystalline diffraction patterns^{13,14,21} and in the 2000's, a group at Lawrence Livermore National Laboratory used electron energy loss spectroscopy (EELS) to investigate electronic structures²²⁻²⁷. Neither group took advantage of the method's small detection limit but either worked with the maximum amounts available to them or started from a bulk sample which was then prepared for TEM using traditional sample preparation methods²³. Recent improvements have made TEM significantly more powerful and it can now even be used to investigate single atoms. Here, we leverage these improved capabilities and complement them with a newly developed workflow that allows working with amounts as small as a single nanogram to explore crystal and electronic structures of Bk and Cf oxides. Both elements are exceedingly rare and expensive and their high radioactivity poses a serious health risk. Further, ²⁴⁹Bk (half-life \approx 330 days) β -decays to ²⁴⁹Cf. Samples thereby self-contaminate and experiments benefit from a fast workflow and, when possible, processing of the samples close to the characterization facility. TEM provides a way to analyze morphology, crystal structure and electronic structure in a safe, cost-effective and rapid manner.

TEM samples of actinide compounds were prepared by dropcasting aqueous acidic solutions of the chloride salts onto the carbon-film side of a standard TEM grid and letting the samples dry at room temperature and ambient pressure (Figure 1 and Supplemental Information, Figure SI 1). Each drop had a volume smaller than 1 μ l and contained between 1 and 10 ng of the actinide. As the liquid evaporated and the drop contracted, the concentration of the solute in the drop rose until it supersaturated and particles precipitated. In an idealized case, one would expect even contraction of the drop and, ultimately, material deposition in a tiny area of the TEM grid. In practice, contact-line-pinning was a dominant factor which caused uneven contraction of the drop and the precipitation of particles on geometrical features (Supplemental Information, Figure SI 1). Prior to working with rare, radioactive elements, we validated the preparation approach using drops containing 1 ng SmCl₃, a non-radioactive surrogate with respect to ion size²⁸ and solubility²⁹. This yielded a carpet of evenly distributed, presumably hydrated, SmCl₃ particles with well-defined facets (Supplemental

Information, Figure SI 2).

We then moved on to experiments with the isotopes ^{243}Am , ^{248}Cm , ^{249}Bk and ^{249}Cf . In contrast to the preliminary experiments, none of the actinides deposited as neatly. We always found large, mostly electron-opaque deposits in the middle of the deposition area which were identified as non-radioactive contaminants (Supplemental Information, Figures SI 3 and SI 4) using energy-dispersive X-ray spectroscopy (EDS) and EELS. The presence of these non-radioactive contaminants in actinide samples reveals another challenge unique to working with actinides: Their production is difficult and often focused on radiopurity rather than chemical purity. The detection of these previously overlooked, non-radioactive contaminants highlights the critical information that can be harvested via electron microscopy and could have large implications on the quality control of rare isotope production and nuclear forensics.

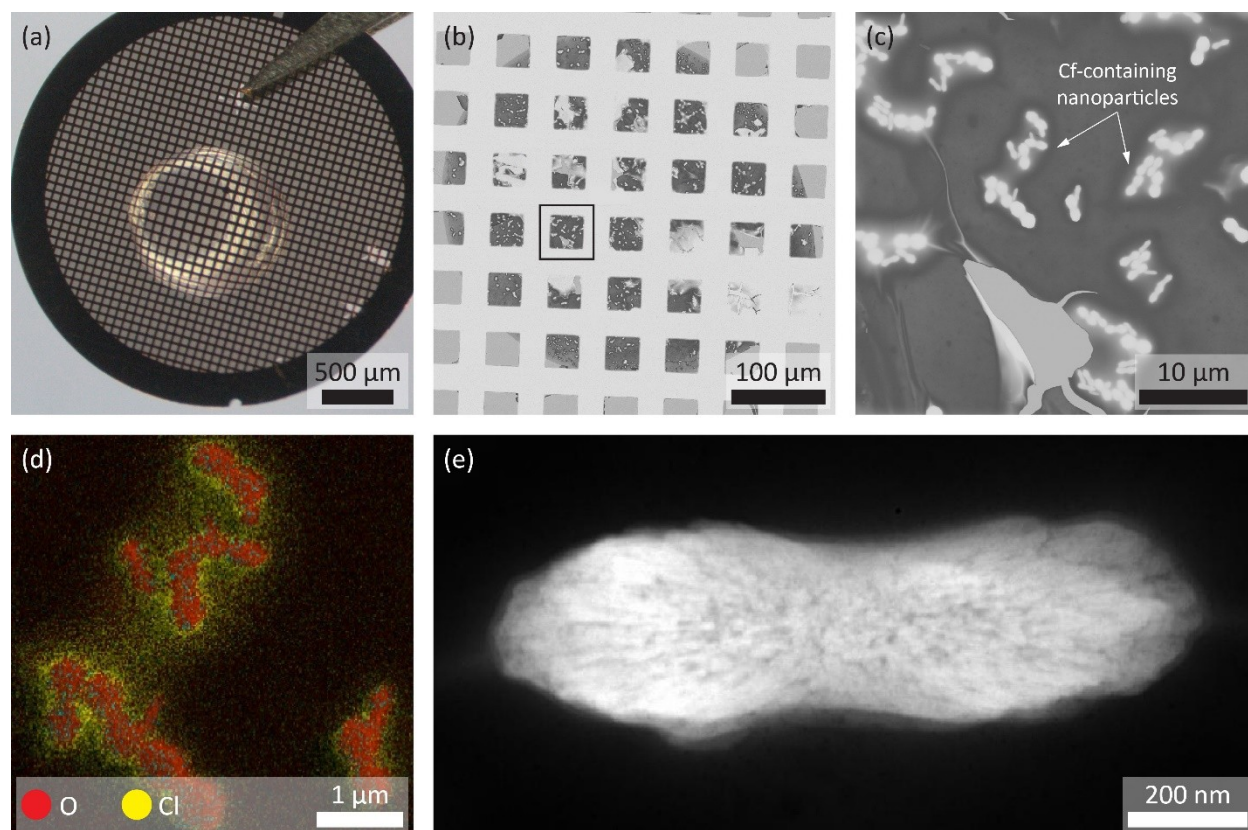


Figure 1: (a) Droplet of a solution containing Cf on a TEM grid. (b) The dried drop is imaged using the STEM detector of an SEM. A box marks the region shown in (c), in which individual particles can be seen. (d) EDS mapping confirms that the particles contain O and have Cl-enriched surfaces. (e)

Individual spectra also confirm that the particles contain Cf (Supplemental Information, Figure SI 5). (e) HAADF-STEM image of individual particles shows the pores.

Cf-containing particles precipitated in a large area and in large amounts. These particles formed with a distinct, dumbbell-like morphology several micrometers in length and had a structure with pores along the long axis of the particle (Figure 1 e). Spectroscopic analysis confirmed the presence of Cf throughout the particle. It also indicated the presence of oxygen (O) throughout the particle and of chlorine (Cl) at the surfaces (Figure 1 d). The particles were beam-sensitive and it was not possible to accurately determine their chemical composition or crystal structure. However, strong Cl, O and Cf signals in EDS spectra suggested the formation of a hydrated chloride material (Supplemental Information, Figure SI 5 a), which is in line with the use of a solution of californium chloride in hydrochloric acid. After extended electron-beam irradiation, a beam-stable, polycrystalline compound formed *in situ* which had strong Cf and O signals in EDS and EELS, but no signs of Cl (Supplemental Information, Figure SI 5 b). Electron diffraction proved challenging due to crystallite size and nearby contaminants, but the structure of the compound as seen in atomically-resolved high-angle annular dark-field (HAADF) STEM images was consistent with trigonal Cf_2O_3 (Figure 2 a) ³⁰. Cf_2O_3 has in the past been prepared by heating CfOCl in water vapor or O_2 ³¹, and we propose that the electron beam irradiation ³² had a similar effect.

In comparison, the sample prepared using the Bk(III) stock solution was significantly more contaminated to the point that contaminants, particularly carbon (C), dominated. However, we were able to directly observe nanoparticles of cubic BkO_2 (Figure 2 b) instead of needing extensive electron beam irradiation ³³. We assume that the electron-beam-induced reaction happened too quickly to witness, as the direct formation of BkO_2 from an aqueous solution is thermodynamically unfavorable. Nonetheless, the beam-induced formation of BkO_2 , with tetravalent Bk, as opposed to Bk_2O_3 , with trivalent Bk, is in line with the relatively low redox potential of Bk(IV)/Bk(III) (+1.60 V in 1 M HClO_4 versus NHE) compared to Cf(IV)/Cf(III) (+3.2 V versus NHE) ^{34,35}.

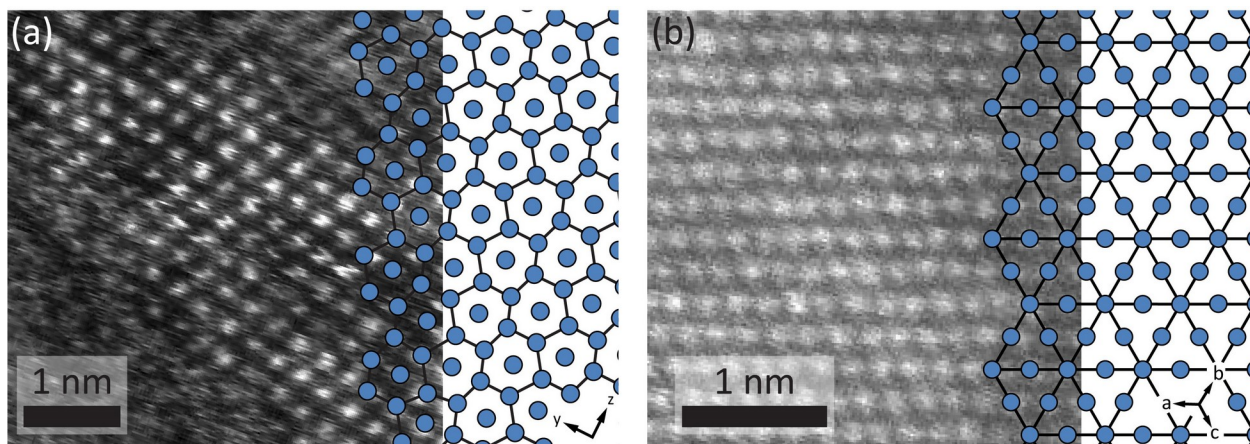


Figure 2: (a) Cf_2O_3 viewed along the $[100]$ lattice vector and partly overlaid schematic showing Cf columns (b) BkO_2 viewed along the $[111]$ lattice vector with Bk atoms shown in the partly overlaid schematic. Please note that O atoms are not visible in the HAADF-STEM images and are therefore not shown in the schematic, either. In the schematics, atoms were connected by lines to accentuate structural motifs.

Absorption edges of the actinides have mostly been observed using synchrotron-based X-ray absorption spectroscopy (XAS), but only a handful of beamlines can accommodate radioactive materials³⁶. Beside the logistical and administrative hurdles, even the microgram amounts required for XAS experiments often represent significant health hazards. EELS garners comparable data²⁴, but excels at much lower energy ranges and requires significantly smaller sample amounts due to the increased beam-sample interactions of electrons compared to x-rays. Moore *et al.* successfully used EELS to study the $\text{O}_{4,5}$, $\text{N}_{4,5}$ and $\text{M}_{4,5}$ edges of several bulk actinide metals up to Cm^{1,25,27} and we now contribute the $\text{O}_{4,5}$, $\text{N}_{4,5}$ and $\text{M}_{4,5}$ edges of Bk and Cf (Figure 3). Previously, only L edges of these two elements were measured using XAS. Initial measurements required hundreds of micrograms per sample³⁷⁻³⁹, although recent optimization reduced the required amount to 1-20 μg per XAS sample⁴⁰. This is, however, still about three orders of magnitude higher than in our experiments.

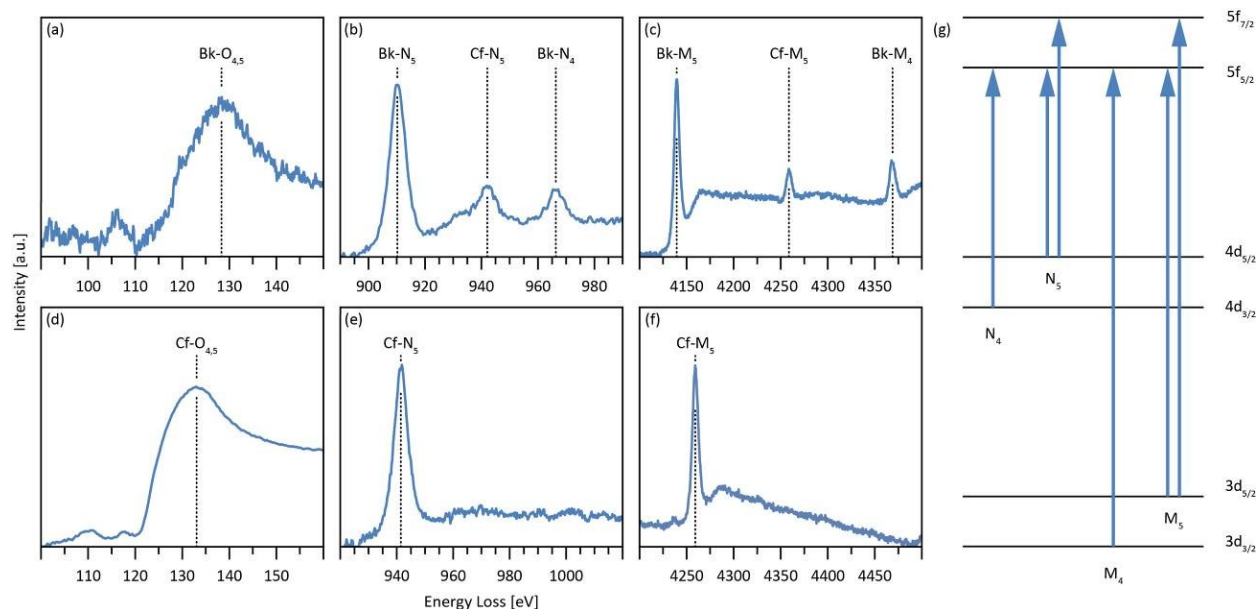


Figure 3: EELS spectra showing the (a) O_{4,5}, (b) N_{4,5} and (c) M_{4,5} edges of Bk and the (d) O_{4,5}, (e) N_{4,5} and (f) M_{4,5} edges of Cf. The spectra of Bk have contributions from Cf that formed by radioactive decay. Please note that the scaling of the energy loss axis differs depending on whether O_{4,5}, N_{4,5} or M_{4,5} edges are shown. It is, however, consistent when comparing specific edges of the two elements. (g) Simple band diagram showing the transitions corresponding to the different white lines.

The O_{4,5} edges measure 5d → 5f transitions, but both the O₄ and the O₅ edges are contained in a broad edge commonly referred to as the giant resonance²². The onsets for Bk (Figure 3 a) and Cf (Figure 3 d) are at energy losses of 110 and 121 eV, respectively. As the ²⁴⁹BkO₂ sample also contained ~15% ²⁴⁹Cf due to the former's radioactive decay, the measured O_{4,5} edge of Bk has a shoulder we ascribe to Cf. However, as the O_{4,5} edge of Bk is at a lower energy loss than that of Cf, its onset should be accurately determined. Both onsets also continue a trend established for the lighter actinides, where the onset shifts by approximately 10 eV from one actinide to the next²⁷. Several peaks with a comparatively weak intensity precede the giant resonance peaks. These could have several causes as described in the Supplemental Information, and we are therefore hesitant to assign physical meaning to them.

In contrast to the O_{4,5} edges, the N_{4,5} and M_{4,5} edges, which result from 4d → 5f and 3d → 5f transitions, respectively, have well-defined onsets and characteristic white lines (Figure 3 g). For Bk, the N_{4,5} (Figure 3 b) and M_{4,5}

edges (Figure 3 c) have two well-defined white lines each. The N₅ and the N₄ edge have maxima at energy losses of 910 and 966 eV, respectively, and the M₅ and the M₄ edge have maxima at energy losses of 4140 and 4368 eV, respectively. In contrast, Cf only has one N₅ white line (Figure 3 e) with a maximum at 942 eV and one M₅ white line (Figure 3 f) with a maximum at 4259 eV but is missing N₄ and M₄ white lines. Due to the decay of ²⁴⁹Bk to ²⁴⁹Cf, the N₅ and M₅ white lines of Cf are also seen in the spectra of the Bk sample, but the edges are not expected to overlap with any features of the Bk edges. In spectra showing the M edges (Figures 3 c and 3 f), each of the white lines is followed by a second, rather broad peak at distances between 30 and 40 eV. These artifacts are likely due to multiple scattering processes involving plasmon excitations.

Of particular interest are the missing N₄ and M₄ edges of Cf, which normally result from the 4d_{3/2} → 5f_{5/2} and the 3d_{3/2} → 5f_{5/2} transition, respectively (Figure 3 g). As electrons always transition from fully-filled d-bands, the intensities of these edges depend entirely on the occupancies of the f_{5/2} band and the absence of the N₄ and the M₄ edge consequently indicates a fully-filled f_{5/2} band. Similar behavior has been observed for metallic Cu^{41,42}. Our results are in line with f-band occupancies calculated from the formal oxidation states that follow from the previously determined chemical compositions⁴³⁻⁴⁷: Cf(IV) with 5f⁸ in CfO₂ and Cf(III) with 5f⁹ in Cf₂O₃. These findings also continue a trend observed by Moore *et al.*, who described a steady decrease in the intensity of the N₄ peak of the actinides until Am and attributed it to a filling of the 5f_{5/2} band under a *jj* coupling scheme (spin-orbit coupling > exchange interaction)²⁶. Moore *et al.* also described a break in this behavior for Cm: Metallic Cm has an f-band occupancy of 5f⁷ and one would consequently expect a fully filled 5f_{5/2} band and suppression of the N₄ peak. Experiments contradicted this expectation, and they rationalized the unexpectedly intense N₄ peak by a shift towards the *LS* coupling scheme (spin-orbit coupling < exchange interaction), leading to electrons filling the 5f_{5/2} as well as the 5f_{7/2} band. We have confirmed their results with oxidized Am and Cm compounds prepared using our experimental approach (Supplemental Information, Figures SI 6 and SI 7), and extend their line of reasoning to our findings. Bk, which in our samples has an expected configuration of 5f⁷ (Bk(IV) in BkO₂) and therefore could fill the f_{5/2} band under a *jj* coupling scheme, behaves similarly to Cm and is shifted towards an *LS* coupling scheme, whereas Cf behaves like the early actinides and adheres to a *jj* coupling scheme.

Experimental observations made in the 1960's and 1970's⁴⁴⁻⁴⁷, and recently confirmed^{10,11,48-50}, indicate that the transplutonium element series, unlike the analogous lanthanide series, is not monotonic. In particular, there is a growing body of evidence showing a pivot starting at Bk and Cf. Previous observations were made via solution thermodynamics experiments (complex formation constants and liquid-liquid extraction behavior), magnetic measurements, density functional theory (DFT) calculations, and structure determinations (extended X-ray absorption fine structure (EXAFS) and single crystal diffraction) with notably shorter-than-expected bond distances in the case of Cf compounds^{5,10,11,40,50}. The fundamental reason for this empirically established inhomogeneity along the series can now be rationalized by the electronic configuration scheme followed by these transplutonium elements as described above.

In this work, we demonstrated the comprehensive analysis of actinide-containing, crystalline particles using amounts, and thereby radioactivity levels, several orders of magnitude lower than with commonly employed methods. By working with such small amounts, we successfully reduced administrative and engineering controls, accelerated workflows, limited the radiological exposure to workers and equipment, used non-dedicated equipment, reduced self-irradiation artifacts, decreased the costs associated with materials procurement and waste disposal, and managed to work with heavily contaminated, yet precious, samples. The comparative study of the f-band occupancies of Bk and Cf yielded an unexpected change in the strength of the spin orbit coupling relative to the exchange interaction and thereby further bolsters the status of Cf as a transitional element within the actinide series. Our approach can be extended to other radioactive materials and allows not only complementing prior studies of the early actinides, but also opens a new avenue for exploring the solid state chemistry of elements such as einsteinium (²⁵²Es and ²⁵⁴Es, respective half-lives: 472 and 276 days), fermium (²⁵⁷Fm, half-life: 100 days), and mendelevium (²⁵⁸Md, half-life: 51 days) for the first time.

REFERENCES

1. Moore, K. T. & Van der Laan, G. Nature of the 5f States in Actinide Metals. *Rev. Mod. Phys.* **81**, 235–298 (2009).
2. McDevitt, M. R. *et al.* Feed-Forward Alpha Particle Radiotherapy Ablates Androgen Receptor-Addicted Prostate Cancer. *Nat. Commun.* **9**, 1629 (2018).

3. Thiele, N. A., Woods, J. J. & Wilson, J. J. Implementing f-Block Metal Ions in Medicine: Tuning the Size Selectivity of Expanded Macrocycles. *Inorg. Chem.* **58**, 10483–10500 (2019).
4. Natrajan, L. S., Swinburne, A. N., Andrews, M. B., Randall, S. & Heath, S. L. Redox and Environmentally Relevant Aspects of Actinide(IV) Coordination Chemistry. *Coord. Chem. Rev.* **266–267**, 171–193 (2014).
5. White, F. D., Dan, D. & Albrecht-Schmitt, T. E. Contemporary Chemistry of Berkelium and Californium. *Chem. - A Eur. J.* **25**, 10251–10261 (2019).
6. Arnold, P. L., Dutkiewicz, M. S. & Walter, O. Organometallic Neptunium Chemistry. *Chem. Rev.* **117**, 11460–11475 (2017).
7. Roberto, J. B. *et al.* Actinide Targets for the Synthesis of Super-Heavy Elements. *Nucl. Phys. A* **944**, 99–116 (2015).
8. Young, J. P., Haire, R. G., Fellows, R. L. & Peterson, J. R. Spectrophotometric Studies of Transcurium Element Halides and Oxyhalides in the Solid State. *J. Radioanal. Chem.* **43**, 479–488 (1978).
9. Peterson, J. R. Techniques of Microchemistry and Their Applications to Some Transcurium Elements at Berkeley and Oak Ridge. in *Lanthanide and Actinide Chemistry and Spectroscopy* 221–238 (1980).
10. Deblonde, G. J.-P. *et al.* Spectroscopic and Computational Characterization of Diethylenetriaminepentaacetic Acid/Transplutonium Chelates: Evidencing Heterogeneity in the Heavy Actinide(III) Series. *Angew. Chemie - Int. Ed.* **57**, 4521–4526 (2018).
11. Silver, M. A. *et al.* Characterization of Berkelium(III) Dipicolinate and Borate Compounds in Solution and the Solid State. *Science* **353**, aaf3762 (2016).
12. Hecker, S. S. The Magic of Plutonium: 5f Electrons and Phase Instability. *Metall. Mater. Trans. A* **35**, 2207–2222 (2004).
13. Baybarz, R. D., Haire, R. G. & Fahey, J. A. On the Californium Oxide System. *J. Inorg. Nucl. Chem.* **34**, 557–565 (1972).
14. Haire, R. & Baybarz, R. Studies of Einsteinium Metal. *J. Phys.* **40**, 101–102 (1979).
15. Krivanek, O. L. *et al.* Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy. *Nature* **464**, 571–574 (2010).
16. Ramasse, Q. M. *et al.* Probing the Bonding and Electronic Structure of Single Atom Dopants in Graphene with Electron Energy Loss Spectroscopy. *Nano Lett.* **13**, 4989–4995 (2013).
17. Ishikawa, R., Shibata, N., Taniguchi, T. & Ikuhara, Y. Three-Dimensional

- Imaging of a Single Dopant in a Crystal. *Phys. Rev. Appl.* **13**, 034064 (2020).
18. Lovejoy, T. C. *et al.* Single atom identification by energy dispersive x-ray spectroscopy. *Appl. Phys. Lett.* **100**, 154101 (2012).
 19. Hage, F. S., Radtke, G., Kepaptsoglou, D. M., Lazzeri, M. & Ramasse, Q. M. Single-atom vibrational spectroscopy in the scanning transmission electron microscope. *Science* **367**, 1124–1127 (2020).
 20. Spurgeon, S. R. *et al.* Nanoscale oxygen defect gradients in UO_{2+x} surfaces. *Proc. Natl. Acad. Sci. U. S. A.* **116**, 17181–17186 (2019).
 21. Haire, R. & Baybarz, R. D. Identification and Analysis of Einsteinium Sesquioxide by Electron Diffraction. *J. Inorg. Nucl. Chem.* **35**, 489–496 (1973).
 22. Moore, K. T. & Van Der Laan, G. Accurate Labeling of the Light-Actinide $\text{O}_{4.5}$ Edges. *Ultramicroscopy* **107**, 1201–1206 (2007).
 23. Moore, K. T. X-Ray and Electron Microscopy of Actinide Materials. *Micron* **41**, 336–358 (2010).
 24. Moore, K. T. *et al.* Electron-Energy-Loss Spectroscopy and X-Ray Absorption Spectroscopy as Complementary Probes for Complex f-Electron Metals: Cerium and Plutonium. *Philos. Mag.* **84**, 1039–1056 (2004).
 25. Moore, K. T., Van Der Laan, G., Wall, M. A., Schwartz, A. J. & Haire, R. G. Rampant Changes in $5f_{5/2}$ and $5f_{7/2}$ Filling Across the Light and Middle Actinide Metals: EELS, Many-Electron Atomic Spectral Calculations and Spin-Orbit Sum Rule. *Phys. Rev. B* **76**, 073105 (2007).
 26. Moore, K. T. *et al.* Emergence of Strong Exchange Interaction in the Actinide Series: The Driving Force for Magnetic Stabilization of Curium. *Phys. Rev. Lett.* **98**, 236402 (2007).
 27. Butterfield, M. T., Moore, K. T., Laan, G. Van Der, Wall, M. A. & Haire, R. G. Understanding the $\text{O}_{4.5}$ Edge Structure of Actinide Metals: Electron Energy-Loss Spectroscopy and Atomic Spectral Calculations of Th, U, Np, Pu, Am, and Cm. *Phys. Rev. B* **77**, 113109 (2008).
 28. Lundberg, D. & Persson, I. The Size of Actinoid(III) Ions - Structural Analysis vs. Common Misinterpretations. *Coord. Chem. Rev.* **318**, 131–134 (2016).
 29. Wilmarth, W. R., Young, J. P., Haire, R. G. & Peterson, J. R. Spectrophotometric Studies of Californium(III) Ions in Selected Lanthanide Trihalide Hosts. *J. Less-Common Met.* **143**, 183–193 (1988).
 30. Baybarz, R. D. High-Temperature Phases, Crystal Structures and the

- Melting Points for Several of the Transplutonium Sesquioxides. *J. Inorg. Nucl. Chem.* **35**, 4149–4158 (1973).
31. Copeland, J. C. & Cunningham, B. B. Crystallography of the Compounds of Cf - II Crystal Structure and Lattice Parameters of Cf Oxychloride and Cf Sesquioxide. *J. Inorg. Nucl. Chem.* **31**, 733–740 (1969).
 32. Egerton, R. F., Li, P. & Malac, M. Radiation damage in the TEM and SEM. *Micron* **35**, 399–409 (2004).
 33. Peterson, J. R. & Cunningham, B. B. Crystal Structures and Lattice Parameters of the Compounds of Berkelium I. Berkelium Dioxide and Cubic Berkelium Sesquioxide. *Inorg. Nucl. Chem. Lett.* **3**, 327–336 (1967).
 34. Stokely, J. R., Baybarz, R. D. & Peterson, J. R. The Formal Potential of the Bk(IV)-Bk(III) Couple in Several Media. *J. Inorg. Nucl. Chem.* **34**, 392–393 (1972).
 35. Nugent, L. J., Baybarz, R. D., Burnett, J. L. & Ryan, J. L. Electron-Transfer and f-d Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (II-III) Oxidation Potential for Each Member of the Lanthanide and Actinide Series. *J. Phys. Chem.* **77**, 1528–1539 (1973).
 36. Shi, W.-Q. *et al.* Exploring Actinide Materials Through Synchrotron Radiation Techniques. *Adv. Mater.* **26**, 7807–7848 (2014).
 37. Antonio, M. R., Williams, C. W. & Soderholm, L. Berkelium Redox Speciation. *Radiochim. Acta* **90**, 851–856 (2002).
 38. Revel, R. *et al.* First Investigation on the L Edges of the ^{249}Cf Aquo Ion by X-ray Absorption Spectroscopy. *Inorg. Chem.* **38**, 4139–4141 (1999).
 39. Galbis, E. *et al.* Solving the Hydration Structure of the Heaviest Actinide Aqua Ion Known: The Californium(III) Case. *Angew. Chemie* **122**, 3899–3903 (2010).
 40. Kelley, M. P. *et al.* Bond Covalency and Oxidation State of Actinide Ions Complexed with Therapeutic Chelating Agent 3,4,3-LI(1,2-HOPO). *Inorg. Nucl. Chem. Lett.* **57**, 5352–5363 (2018).
 41. Leapman, R. D., Grunes, L. A. & Fejes, P. L. Study of the L_{23} Edges in the 3d Transition Metals and their Oxides by Electron-Energy-Loss Spectroscopy with Comparisons to Theory. *Phys. Rev. B* **26**, 614–635 (1982).
 42. Pearson, D. H., Ahn, C. C. & Fultz, B. White Lines and d-Electron Occupancies for the 3d and 4d Transition Metals. *Phys. Rev. B* **47**, 8471–8478 (1993).
 43. Baybarz, R. D. Dissociation Constants of the Transplutonium Element

- Chelates of 1,2- Diaminocyclohexanetetraacetic Acid. *J. Inorg. Nucl. Chem.* **28**, 1055–1061 (1966).
44. Baybarz, R. D. Dissociation Constants of the Transplutonium Element Chelates of Diethylenetriaminepentaacetic Acid (DTPA) and the Application of DTPA Chelates to Solvent Extraction Separations of Transplutonium Elements from the Lanthanide Elements. *J. Inorg. Nucl. Chem.* **27**, 1831–1839 (1965).
 45. Baybarz, R. D. Separation of Transplutonium Elements by Phosphonate Extraction. *Nucl. Sci. Eng.* **17**, 463–467 (1963).
 46. Gavrilov, K. A., Gvzdz, E., Starý, J. & Seng, W. T. Investigation of the Solvent Extraction of Californium, Fermium and Mendelevium. *Talanta* **13**, 471–476 (1966).
 47. Hubert, S., Hussonnois, M., Brillard, L., Goby, G. & Guillaumont, R. Determination Simultanee de Constantes de Formation de Complexes Citrique de l’Americium, du Curium, du Californium, de l’Einsteinium et du Fermium. *J. Inorg. Nucl. Chem.* **36**, 2361–2366 (1974).
 48. Drader, J. A., Luckey, M. & Braley, J. C. Thermodynamic Considerations of Covalency in Trivalent Actinide-(poly) aminopolycarboxylate Interactions. *Solvent Extr. Ion Exch.* **34**, 114–125 (2016).
 49. Kelley, M. P. *et al.* Revisiting Complexation Thermodynamics of Transplutonium Elements up to Einsteinium. *Chem. Commun.* **54**, 10578–10581 (2018).
 50. Cary, S. K. *et al.* A Series of Dithiocarbamates for Americium, Curium, and Californium. *Dalt. Trans.* **47**, 14452–14461 (2018).

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CONTRIBUTIONS

This work combined two disciplines: actinide chemistry, represented by G.J.-P.D. and R.J.A., and electron microscopy, represented by A.M., P.A.E., S.E.Z. and A.M.M. This work would not have been possible without many discussions throughout which open questions in the field of actinide chemistry were combined with the capabilities offered by electron microscopy, thereby setting the scope of this manuscript. G.J.-P.D. prepared the samples and optimized the dropcasting process. A.M., P.A.E. and S.E.Z. performed the scanning electron microscopy and transmission electron microscopy experiments. A.M. analyzed the data. All authors contributed to the writing and editing of this manuscript.

DATA AVAILABILITY STATEMENT

All relevant images and spectra analyzed during this study are included in the article and its supplementary information. Raw data is available from the corresponding author on request.