Effect of temperature and radiation damage on the local atomic structure of metallic plutonium and related compounds

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\textbf{ABSTRACT}

This focused review provides an overview and a framework for understanding local structure in metallic plutonium (especially the metastable fcc $\delta$-phase alloyed with Ga) as it relates to self-irradiation damage. Of particular concern is the challenge of understanding self-irradiation damage in plutonium-bearing materials where theoretical challenges of the unique involvement of the $5f$ electrons in bonding limit the efficacy of molecular dynamics simulations and experimental challenges of working with radioactive material have limited the ability to confirm the results of such simulations and to further push the field forward. The main concentration is on extended X-ray absorption fine-structure measurements of $\delta$-phase Pu, but the scope is broadened to include certain studies on plutonium intermetallics and oxides insofar as they inform the physics of damage and healing processes in elemental Pu. The studies reviewed here provide insight into lattice distortions and their production, damage annealing and defect migration, and the importance of understanding and controlling sample morphology when interpreting such experiments.

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1. Introduction

The purpose of this article is to review local structure measurements made by the extended X-ray absorption fine-structure (EXAFS) technique of self-irradiation damage that emphasize fundamental issues in understanding radiation damage in metallic plutonium, while considering other related materials that can shed light on these issues where a paucity of Pu data exists. As such, we will focus on relatively simple metals, and the simplest, most important, and most studied metallic phase is the metastable $\delta$-phase of Pu alloyed with Ga [1]. Certain studies of intermetallics and oxides are also reviewed to provide a more complete picture of the observed effects in metallic Pu, and other materials are also considered when necessary for historical or other reasons.

Understanding the consequences of self-irradiation damage, that is, damage caused by the radioactive decay of a constituent element, has important scientific and technological implications. Radioactive materials, be they natural minerals, those involved in nuclear power generation, or part of the nuclear weapons stockpile, are constantly degrading due to the changing chemistry from the transmutation of constituent elements via radioactive decay and the effects of energetic particles involved in this decay. Such effects in minerals have been recognized since the late 19th century and dubbed ‘metamictization’ [2]. Self-irradiation damage can be a much more rapid process in materials with man-made isotopes, and indeed was recognized as a performance issue in the earliest nuclear reactors. Initially, radioparagenesis was identified as the major issue with neutron absorbers produced as part of the fission process [3], but other effects were soon recognized and careful experimental studies were being performed on electronic and lattice effects, void swelling, etc. [4–6]. Such studies continue today in the nuclear power generation industry. Likewise, concerns around the viability of an aging nuclear weapons stockpile have grown in this era of the Nuclear Test Ban Treaty, underscoring the need for understanding damage from both technological and fundamental points of view [7,8].
By the late 1940s, theories of the lattice response to the radioactive decay process were being developed. The early theories focused either on the macroscale heating response [5] or on microscale ballistic events [9]. In the work discussed below, which focuses on metallic plutonium, the uranium recoil nuclei from $\alpha$-decay of common Pu isotopes causes most of the damage, which are typically in the 80–90 keV range. Today’s best models in this energy range are rooted in the ballistic theory of Nobert, Robinson, and Torrens [10] coupled with molecular dynamics (MD) methods that account for the effect of the ballistic events on many thousands of atoms in an attempt to understand the macroscale implications. More energetic heavy ions need to be included in certain other situations [11,12], for instance, for heavy fission fragments, but are not considered further here.

While such theories have had success in understanding properties such as the increased electrical resistance due to defect scattering, lattice parameter and volume changes, and helium bubble formation, fundamental computational limits exist that prevent a complete understanding of this complex problem, particularly for materials containing plutonium. The biggest limitation is the large number of atoms required to fully characterize a damage event in an accurate simulation. This limitation is partially overcome by performing calculations at elevated temperatures, thereby taking advantage of annealing processes to reduce the number of displaced atoms per decay event. The second limitation is the paucity of good potentials for actinides, especially plutonium. This paucity is particularly problematic in light of the incredibly complex bonding that $5f$ orbitals produce. For example, even simplifying the problem by focusing on elemental Pu requires a potential that can mimic all 6 phases that occur before melting in the ambient-pressure phase diagram [1], including the monoclinic $\alpha$-phase, which has 8 unique Pu sites in its unit cell [13]. The combination of these factors, together with the safety requirements and, sometimes, the security requirements involving experiments with radioactive materials, make experimental verification of these calculations difficult.

In order to rely on MD simulations for a microscopic understanding of self-irradiation damage, a microscopic verification is still necessary. Local structure methods should be able to provide such verification, since they provide radial distribution function (RDF) measurements that can be compared to those obtained in the simulations. Since these RDFs are inherently normalized to the number of atoms in a material, they avoid some of the pitfalls of other experiments, such as conventional diffraction experiments that rely on crystalline order to make quantitative comparisons, and are therefore plagued by the inherent disorder at all length scales in the present problem. Pair-distribution function analysis of total scattering data is such a local structure technique [14], but has only been applied sparingly to understanding radiation damage (e.g. [15–18]), especially in Pu materials [19]. On the other hand the EXAFS technique has been applied much more consistently to materials damaged by irradiation for the last 35 years, including a reasonable number on Pu metal and intermetallic studies, and so this
review focuses on EXAFS studies. There has, in fact, been a recent surge in such measurements of nuclear energy materials in general, such as fuels [20–22] and fuel cladding and other materials (e.g. [23–25]), and even ion implanting in the semiconductor industry [26], not to mention a long history of such studies of nuclear waste forms (for a recent example, see Ref. [27]). While that literature is growing rapidly (we have only cited a few examples), the concern of this review is the less-studied topic of damage in plutonium metal and related materials, especially as can potentially be related to present and future calculations of the local structure.

This short review is not intended to be comprehensive; rather, it aims to highlight certain features of what EXAFS has taught us about radiation damage in general and defect production and migration in particular. In fact, radiation damage on a microscopic level cannot be understood without also separating and understanding annealing properties and the complicating role of sample morphology. Therefore, the major themes of the results digested below are (1) understanding and quantifying lattice distortions and their production, (2) using annealing properties to discern healing properties and defect migration, and (3) to account for the role of morphology and sample history effects in determining radiation damage effects.

This review continues with a brief account of theory as it relates to the local structure issues in metallic plutonium while contrasting the physical processes with those in other materials, followed by a description of some key related experiments that focus on structural and/or annealing effects, before presenting the contributions of the local structure studies.

2. Related background and theory

The following narrative focuses on atomic-level, short-range structural calculations, and does not consider, for example, more macroscopic phenomena such as void swelling and bubble formation. Such macroscopic effects generally have a relatively small effect on local structure. While focusing on Pu metal calculations, some other calculations are presented that help provide context for understanding the Pu calculations.

Although β- and γ-decay events damage material, α-decay events are the most damaging in Pu decays, primarily due to the high momentum of the large recoil nucleus (for a basic review, see Ref. [28]), as well as the relative availability of the 239Pu isotope, which decays primarily through α-decay. As diagrammed in Figure 1(a), this nucleus ballistically interacts with other atoms in the lattice, typically only losing a small fraction of its kinetic energy each time it knocks a neighboring atom from its ideal lattice position. To illustrate these effects, a simplified model can be employed, but bear in mind temperature and lattice effects are not considered in any detail in this model. In the case of elemental plutonium, the energy required to displace an atom, ED, is estimated to be about
14 eV, while the average recoil kinetic energy for, say, a $^{235}$U nucleus from the $\alpha$-decay of $^{239}$Pu, is 86 keV. Accounting for a range of collision angles (glancing blow, head-on, etc.), an average of about 2290 defect pairs produced for each decay can be estimated at the end of a $\approx 12$ nm recoil range in a cascade of about 7.5 nm in diameter using a simple procedure outlined by Robinson [29]. In contrast, the range of the $\alpha$ particle is about 10 $\mu$m in $\delta$-Pu, but most of its energy is dissipated by electronic excitations, and only about 265 displacements are produced at the end of its range in a region with an average diameter of 0.8 $\mu$m [28].

Within this simplified approach, details of the lattice response to these defects are not included, nor are any finite temperature effects, and such effects can be substantial. More generally in metals, Diaz de la Rubia et al. [30] have shown that defect migration reduces these defect estimates substantially in Au, with only $\approx 66\%$ of the defects expected from the linear theory similar to above [10] not recombining with vacancies at 50 K for a 10 keV Au cascade, and only 6% surviving at 300 K. Such calculations, in fact, support resistivity studies of Cu and Ag [31].

While considering damage effects in Pu metals, it is important to contrast damage mechanisms to those that occur when more covalent and directional bonding can occur. For example, strong distortions around Ga in Pu:Ga alloys may mimic such bonding, or impurities in a metal may otherwise have different damage properties and affect the damage in the host material. Another reason to consider such bonding is that Pu is a strongly correlated material, which indicates that local bonding can occur due to hybridization between the conduction band and the local $f$ density of electronic states (e.g. Ref. [32]). In addition to the studies on metals mentioned above, Diaz de la Rubia et al. [30] also demonstrated that very different kinds of damage production in materials occurs with strong covalent bonding, which was explored to good effect by Veiller et al. who reported MD simulations of $\alpha$-recoil damage in zirconolite [33] with good qualitative agreement of RDFs with EXAFS experiments [34–37]. The main difference with covalent bonding in damaged material was illustrated well by Trachenko [38,39], who modeled this situation for zircon, as shown in Figure 1(b), demonstrating the strong propensity for nearest-neighbor oxide octahedra to reform even in heavily damaged regions.

Considering such effects in plutonium remains a difficult research topic, partially owing to Pu’s ability to form so many different structures, but it has been well established that the effect of temperature on defect migration and recombination is substantial. Kubota et al. [40] report detailed simulations of defect production and lattice response at temperatures ranging from 180 to 600 K as a function of time. Figure 2 shows the defect production as a function of time in $\delta$-Pu at two different temperatures. The lowest temperature simulation demonstrates a fundamental constraint on such calculations, as the number of defects diverges with time. As will be seen in Section 3, most defects are, in
Figure 1. Examples of damage effects from energetic recoil nuclei. Notes: Panel (a) depicts defect pair production in δ-Pu from the α-decay of a 239Pu nucleus into an 86 keV 235U nucleus and a 5 MeV α particle, emphasizing the dominant damage production of the recoil nucleus. Panel (b) shows a slice through a region suffering from two overlapping damage events in zircon from 50 keV U nuclei. These results emphasize the strong ability of covalently bonded systems to reorder locally.

fact, annealed out by 180 K, so this divergence is likely far less severe than at lower temperatures, although this discrepancy is likely due to possible α-phase growing in as a consequence of the perturbation to the system where no Ga exists in the calculation to stabilize the δ-phase. Interestingly, the room temperature calculation finds a nearly steady-state (comparatively) number of defects produced (≈2000 per decay), which is noted to be much higher than expected for a 20 keV 235U recoil nucleus. Another distinctive feature of this study is the reporting of the RDF (Figure 2(c)) and the strong damping of the local structure: within a damage cascade over 15 nm containing about 90,000 atoms, this defect density corresponds to about 3% of the atoms within a cascade. The pair correlation function, however, is reduced by about 50%, demonstrating the overwhelming role that lattice distortions around the defects play in the overall crystal structure. Kubota et al. note that this strong lattice response may be due to formation of local structures different than δ-Pu that are either stable or long-lived.

Clearly, advances in MD methods have the potential to revolutionize understanding of radiation damage, and an important future goal for this kind of work with Pu is to directly compare RDFs to the MD results as has been accomplished for other disordered systems. For instance, modeling liquid structures in systems where the interatomic potentials necessary for MD simulation are well known, the agreement between calculated and simulated RDF is remarkable [41]. Such methods have also been applied to damaged materials such as metamict zircon [42] with success. In order to decouple the separate issues of damage production and annealing, either vastly more powerful computational methods will need to be employed to allow calculations on large-enough numbers of atoms to fully
Figure 2. Examples of defect production for a 20 keV $^{235}$U recoil nucleus at 300 and 180 K, together with representative pair correlation functions (RDFs). Note that the number of defects reaches a steady state in the 300 K simulation and diverges in the 180 K simulation. Another simulation (not shown [40]) finds that most defects are removed at these time scales at 600 K. From Ref. [40].

contain a damage cascade at low temperatures, or better approximation methods will need to be developed [43].

3. Related experiments

Local structure methods, while applied in some early total scattering experiments on radiation damaged materials (e.g. Ref. [15]), were rarely employed for that purpose until the late 1970s and early 1980s with the advent of EXAFS techniques (early technique development includes, e.g. Ref. [44–46], for an overview of EXAFS techniques, see Ref. [47,48]). The main experiments used for studying radiation damage effects were and still are X-ray diffraction (XRD), strain-gauge measurements of volume, and electrical resistivity. As described in this section, electrical resistivity measurements proved to be perhaps the most useful, since changes in resistivity could be attributed to the scattering centers generated by defect formation, although without truly atomic-level structural probes, this amounted to using an untested theory (defect formation due to
radiation damage) with an untested experimental technique (attributing all the change in resistivity as due to defects). In any case, obtaining defect densities or damage fractions from diffraction data turned out to be problematic due to the complex morphology of plutonium. These early experiments still encapsulate most of our knowledge of the effects of self-irradiation on plutonium materials.

The first measurements demonstrating the effect of radiation damage on resistivity in Pu are likely those reported by Lee et al. [49], followed by the first temperature-dependent resistivity measurements demonstrating the annealing properties [50]. Similar effects were noted in lattice parameter measurements by Lallement and Wigley [51], and later by Jacquemin et al. [52] who found a 1.2% contraction in δ-Pu after about 2500 h, while β-Pu only contracted about 0.07% after 1800 h, and appeared to be leveling off. Averback et al. [31] performed a seminal work making the first comparison of simulated defect concentrations to those determined from resistivity data.

More recently, Fluss, McCall and coworkers [53–55] reported isochronal annealing studies of α- and δ-Pu, measuring both resistivity and magnetic susceptibility (Figure 3(a)). Although obvious differences exist between the annealing curves of the two quantities, especially for α-Pu, they display similar qualities. The curves are segregated into 5 annealing stages [56]. Focusing on the δ-Pu data, Stage I–II are attributed to interstitial mobility and annihilation, and Stages III–V are similarly attributed to vacancy annihilation. The large difference in Stage I annealing between the resistivity and magnetic susceptibility data from δ-Pu is attributed to more frequent trapping of mobile interstitials in the lower density δ-Pu system, together with the hypothesis that magnetic susceptibility is not as sensitive to interstitials as resistivity. Finally, resistivity and susceptibility for δ-Pu and the lack of such a difference between the resistivity and magnetic susceptibility data in α-Pu, as shown in Figure 3(a), suggests that Ga interstitial migration occurs more easily than Pu interstitials in δ-Pu and has a larger effect on resistivity.

There are two other important features of the susceptibility data when the sample was held within annealing Stage I (below 30 K). The first is the observation of magnetic moments in damaged δ-Pu, indicating that δ-Pu is near a magnetic phase boundary and that short-range magnetic correlations may exist in the undamaged material. This hypothesis has since been supported by neutron scattering measurements [32]. The second feature is the ability of susceptibility in this case to be used to estimate the fractional volume of the sample contributing to the magnetic moment, namely 13,600 nm$^3$ per decay, or $\approx$550,000 atoms, or a sphere of about 24 nm average diameter. While the number of atoms far exceeds any estimates of the number of defects, the effective diameter is in reasonable agreement with MD simulations of the overall size of the cascade. These data therefore suggest that all the atoms within a damage cascade contribute to the moment. As we will see below, this is consistent with each defect causing a
significant distortion of at least the nearest and the next nearest neighbors, as shown in Figure 3(b).

As mentioned in Section 2, contrasting results to those from simple systems where covalent bonding dominates the structure is important, and for that purpose we choose plutonium dioxide as a simple example here. Lattice parameter expansion in PuO$_2$ was noted by Rand, Fox, and Street [57] in samples kept at room temperature reaching $\Delta a/a \approx 0.001$ after nearly 400 days. Turcotte and Chikalla [58] reported lattice parameter changes (using XRD) in PuO$_2$ from room temperature up to nearly 1873 $^\circ$C, with nearly all of the damage recovered by about 1073 $^\circ$C in all measured samples with some notable sample dependencies. Isochronal annealing was performed on various PuO$_2$ samples, and Turcotte and Chikalla [58] attribute an annealing step below 400 $^\circ$C to the removal of interstitials, and a step above 600 $^\circ$C to the removal of vacancies, however, they concede that explanation is an oversimplification since the real lattice contains interstitials and vacancies at both the plutonium and oxygen sites, along with more complex defect clusters. In a damage ingrowth experiment, Chikalla and Turcotte [59] observed that the lattice parameter follows an exponential growth curve for well annealed samples, but exhibits a maximum for samples which are poorly annealed and contain helium or other impurities which could serve as defect sinks. Noe and Fuger [60] repeated these experiments on samples which were freshly prepared, in order to minimize the interference of helium sinks, and observed a similar two-stage isochronal anneal, but note that the distinction between the steps is less clear in samples with less helium, further showing how sample history and stoichiometry changes due to radioactive decay must be kept in mind during any interpretation of results. Another damage recovery stage is identified at 54 K by Jacquemin [61] in strain gauge experiments reaching down to 4.2 K. The change in lattice parameter from 4.2 to 54 K is $\approx$0.0013 Å, and the change up to 1173 K is $\approx$0.014 Å [60]. Turcotte and Chikalla [58] suggested schematically that about half the damage was recovered in the 54 K annealing stage. However, the lattice parameter change is much smaller at this transition than the changes observed above room temperature, suggesting the change at 54 K is due to only about 10% of the damage recovery observed between room temperature and 1173 K. On the other hand, the f electrons in metallic Pu offer additional complications on damage ingrowth. Jacquemin [61] reports that over the first few thousand hours at close to liquid helium temperatures $\alpha$-Pu has an initial length expansion of $4.4 \times 10^{-6}$/h, while metastable $\beta$-Pu and Al stabilized $\delta$-Pu both exhibited contractions of $-2 \times 10^{-6}$/h and $-4.7 \times 10^{-6}$/h, respectively. Transformations to the denser $\alpha$-Pu were ruled out as a cause for the transformation, rather, Jacquemin proposes the possibility that interstitial trapping sites, together with a strong vacancy relaxation effect, could be responsible, the latter being a strong function of the amount of electron transfer [61]. At some point, the role of larger defect structures overcomes the initial contraction phase, and stabilized $\delta$-Pu
Figure 3. (a) Isochronal annealing results for both resistivity and magnetic susceptibility for α- and δ-Pu. From Ref. [55]. (b) Example of atomic displacements for the first ten coordination shells around a tetrahedral interstitial.

Notes: (b) Displacements are taken from a simulation of fcc iron as reported in Beeler [64], which reported the displacement of atoms displaced by more than 1.5% of the lattice constant. Original atomic positions (dark green spheres) are shown with their new relaxed positions (light green spheres) after the addition of an interstitial atom at (1/4, 1/4, 1/4) (red sphere). The displacements range from 0.24 Å in the first coordination sphere to 0.08 Å in the ninth coordination sphere. Note that distortions away from the viewer will be obscured by the original atomic positions.

4. EXAFS experiments

In this section, we review a portion of the EXAFS literature on self-irradiated actinide metals, with oxide materials reviewed for contrast and to provide a more complete physical picture. We include a discussion of zirconate-related materials, as the results directly relate both to the physics of what occurs in the metals and to the history of the subject.

4.1. Plutonium oxides and related oxides

Perhaps the first EXAFS study looking at local structure changes due to self-irradiation was provided by Gregor et al. [34,65], who studied Ti K-edge EXAFS on metamict materials as a function of annealing. This work was important because it provided evidence that both the local atomic and electronic structural changes in such damaged materials could be observed with EXAFS and X-ray absorption near-edge structure (XANES) techniques. These and follow-up studies are the precursors to Ewing and co-workers’ explorations of pyrochlores as
wasteforms utilizing ion implantation and annealing effects on local structure [66–69], which, like the isochronal annealing studies in Section 3 determine the amorphization/recrystallization temperature in certain pyrochlores as an important parameter in evaluating them as high-level radioactive waste forms. These include Greegor et al. [66], which reviewed the usefulness of EXAFS in radiation damage studies by that group in the 1980s, comparing titanium oxides of metamict $AB_2O_6$ blomstrandine, Pu-doped zirconolite $CaZrTi_2O_7$, and $50/200$ keV Pb ions implanted into $SrTiO_3$.

Work in this vein continued with Hess et al. [70,71], who reported the local structure changes in more self-irradiated samples measured with EXAFS, namely, aged Pu-doped glass and ceramic waste forms as a function of accumulated dose. This work utilized three otherwise identical Pu-doped borosilicate glasses aged 15 years, but with different $^{238}\text{Pu}/^{239}\text{Pu}$ ratios to provide samples with consistent morphology and sample histories, yet with variable dose. The main result of this work is that cations with short cation-oxide bond lengths show little damage compared to those with longer oxygen bonds indicating a propensity to reform local structures, possibly consistent with the more directional bonding and subsequent reformation when damaged considered by Trachenko [38,39]. This work was extended further by Begg et al. [68] who reported EXAFS results on the same samples, now aged 18 years with total dose between $1.2 \times 10^{17}$ $\alpha$-decays/g and $2.8 \times 10^{19}$ $\alpha$-decays/g, but in this case both before and after high-temperature anneals in air of $1000$ and $1200$ $^\circ$C. This technique allowed for the observation of Pu(III)$\rightarrow$Pu(IV) oxidation coupled with a decrease in the lattice distortion due to the Pu(III)$\rightarrow$Pu(IV) ionic radius shift on the Zr(IV) site. The amorphous $^{238}$Pu-substituted zircon demonstrated a distorted zircon local structure, which was recrystallized after the $1200$ $^\circ$C anneal, while annealing at $1000$ $^\circ$C resulted in decomposition into constituent oxides.

While most of the emphasis of EXAFS studies of radiation damage effects on oxide materials has been placed on pyrochlores and zircons, recent work includes EXAFS studies of the simple actinide dioxides, irradiated UO$_2$ [72] and self-irradiated AmO$_2$ [22]. The UO$_2$ studies are intriguing as a consideration of the effect of strong covalent bonding because oxygen defect clusters are observed with clear evidence of uranyl U = O bonds at distances of ≈1.8 Å. The study of AmO$_2$ is unique in that the XANES from the recoil nucleus is obtained, in this case due to 6% Np content, although the spectra are consistent with NpO$_2$, as expected. Increases in the first two coordination shells are found to be consistent with the unit cell expansion from XRD of 0.3% in this sample with ≈ $1.4 \times 10^{20}$ $\alpha$-decays/g. In addition, a significant reduction in the EXAFS amplitude from the first 2 shells is observed (about 30%).

4.2. Elemental plutonium and intermetallics

Local structure studies of actinide metals and intermetallics are all, by definition, studies of the effects of self-irradiation damage, although such a focus is not
always employed. For instance, consider studies of Ga-stabilized (i.e. metastable [73,74]) δ-Pu. The role of Ga in partially stabilizing the δ phase remains an active area of research, and Ga may, in fact, also play a role in preserving the δ structure against radiation damage. Work by Conradson and co-workers represents probably the earliest and longest work in this area. Although much of this work has only recently been published in an exhaustive recitation (see below), consideration of damage effects began with the first EXAFS study of δ-Pu by Cox et al. [75], with consideration of how the large Ga-Pu distortion measured by Ga K-edge EXAFS should generate large strain fields which would maximize the number of Pu nearest neighbors around each Ga atom. To achieve this local environment, Ga may then form superlattices in δ-Pu, possibly into regions of Pu$_3$Ga. The local Ga environment was further explored by Faure et al. [76] in a Ga K-edge study of a series of δ-Pu with Ga concentrations ranging from about 1–10 at% and including Pu$_3$Ga itself, showing that the Ga-Pu distance remains constant within about 0.04 Å, similar to the Ga-Pu distance in Pu$_3$Ga, and therefore deviates from Vegard’s Law [77] across the entire Ga-stabilized δ-Pu range. (The observation of such deviations in doped-semiconductors was an early triumph of the EXAFS technique [78]). This work was expanded and clarified by Conradson et al. [19], demonstrating that the Ga-Pu distance remains constant within 0.01 Å from 1.7 to 6.5 at% Ga. Likewise, and perhaps more surprisingly, the Pu–Pu distance also remains constant within 0.01 Å over the same Ga concentration range. Such considerations are threads that run through several other subsequent EXAFS studies of elemental Pu by Conradson et al. [19,79] and Allen et al. [80,81].

Over the subsequent decade, Conradson and co-workers performed multiple studies of different materials with a range of Ga concentrations and ages/doses, that is, a range of time since the sample’s most recent anneal. Some of this earlier work is available [82–85], but the complexity of the problem required a larger study, and consequently was not published until 2014 [79]. In this latter work, δ-Pu samples with ages up to 45 years were studied, including a variety of Ga concentrations and 1.7 at% Ga samples enriched with $^{238}$Pu to act as ‘accelerated’ aged samples due to the higher activity of $^{238}$Pu relative to the more common $^{239}$Pu isotope. A goal of the study was to better understand the pinning effects of potential Ga clusters which may form regions of self-organization, and they note that at least in the low-Ga end of the phase diagram, the close proximity to the martensitic α’ phase argues that exact morphology and sample history are crucial in determining structures, while Pu$_3$Ga precipitates at about 10% Ga. The data show little reduction in the EXAFS amplitude from the Ga edge in samples with Ga content ranging from 1.7 to 3.3 at% that are naturally aged from 15 to 36 years (Figure 4). This result was also observed by Booth et al. [86] as described below, where it was noted to likely indicate gallium’s role in helping prevent damage in δ-Pu as a function of age. Changes in Pu amplitudes in naturally aged samples are smaller than the sample variability
Figure 4. EXAFS data from both naturally aged (top panel) and accelerated aged (from the Accelerated Aging program, or AAP, higher $^{238}$Pu content, shown in the bottom two panels) samples at various Ga concentration.

Notes: (Inset) Fit residuals using a standard fcc model for $\delta$-Pu. The residuals indicate the existence of local structures that vary with time and Ga concentration, including a recurring component named the $\sigma$-phase, which is primarily indicated by strong scattering between 3.8 and 4.0 Å. Both figures are derived from those in Ref. [79].

both between samples with different Ga concentrations and among those with the same concentration; however, clear amplitude reductions are observable in accelerated-aged samples after equivalent decades in some samples, indicating that the irradiation rate is possibly as important as the total dose when it comes to understanding accelerated-aging studies.

An important point raised by Conradson et al. is that the observed changes in the EXAFS spectra with dose/time are generally a function of the radial pair distance $R$ (the distance from the absorbing atom to a near neighbor), consistent with the growth and loss of ordered structures, as shown in the inset of Figure 4. Coupled with their measured XRD patterns that show no significant momentum-dependent transfer of scattering weight from the Bragg peaks to the diffuse scattering background, they conclude that the radiation damage is forming ordered structures that diffract poorly, possibly because they are below the diffraction size limit. The most dominant, non-fcc structure is indicated by an EXAFS peak corresponding to Pu–Pu scattering between 3.8 and 4.0 Å, a feature which has also been measured by other groups [86], as well as by XRD and PDF
measurements [19], and has been dubbed by Conradson [84] as due to a so-called ‘σ-phase.’ However, probably the most important conclusion is reached from the observation of so much variability between samples of different ages, total doses (both natural and accelerated), and Ga concentrations: The EXAFS sample history is vitally important to understand this situation any further, not unlike the situation with the martensites.

While direct studies on δ-Pu are important, studies of other Pu intermetallics offer other ways to understand local structure effects of self-irradiation damage. Booth et al. [87,88] measured radiation damage using EXAFS for room-temperature-stored PuCoGa$_5$, a 18.5 K superconductor [89]. Damage is quantifiable in these data by assuming a fraction of the sample is essentially amorphous with respect to the EXAFS amplitude (does not contribute) and the rest is fully crystalline, and can be modeled nearly equivalently by either simply taking the ratio of the amplitude of the EXAFS peaks individually or by fitting the data to obtain the number of neighbors under each EXAFS peak. It is noted, however, that enhancements in the Debye–Waller factors observed in the latter method likely indicate a surface-to-volume reduction effect at the edges of the still-ordered crystallites that is not properly considered. The amount of damage observed far outpaced the damage rate in δ-Pu (Figure 5(a)). The amount of damage could not be understood in terms of simple defects, but could be explained if significant distortions (> 0.1 Å) occur around the defects including the nearest neighbor shell and a small effect on the next shell, in which case every atom in the damage cascade would experience a significant displacement from its equilibrium position (Figure 3(b)). Such distortions would be large enough to reduce the EXAFS amplitude consistent with practically every atom within the volume of a cascade experiencing a large distortion, analogous to Seitz’s original melting model of radiation damage [5] and consistent with simulations [40] and the SQUID damaged volume measurements [54]. An important feature of this work is that since the damage rates are fast enough to observe changes in the EXAFS multiple times within a single year, data can be collected on the same samples, providing direct comparisons that remove much of the sample variability in the measurements discussed above. The enhanced damage rate over simple defect models is consistent with the conclusions of magic-angle spinning nuclear magnetic resonance experiments reported for zircons [90–92].

Further work comparing individual samples was extended to other Pu intermetallics (PuCoIn$_5$, PuAl$_2$, Pu$_2$PtGa$_8$, PuPt$_2$In$_7$, and PuGa$_3$) to compare to PuCoGa$_5$ and to δ-Pu samples, one of which was held below 30 K for two months to retain more damage. The main feature of this study was to consider the role of annealing in reducing measured damage, both as a function of the stiffness of the lattice (as measured either by the Debye–Waller factors or the material’s melting point) and as a function of temperature. The results shown in Figure 5(b) show a range of damage rates, with δ-Pu data showing the least damage (not shown are Ga K-edge data, which are consistent with even less
damage, as in Ref. [79]) and PuCoGa$_5$ data showing the most damage for those samples stored at room temperature. The general trend roughly correlates with lattice stiffness. The fastest damage accumulation is observed for the δ-Pu sample stored below 30 K. The damage rates are all modeled using a single rate constant for the number of distorted atoms created per decay per atom in the formula unit of 90,000 atoms/decay, and one or two rate constants to describe the annealing (Figure 5(b)). As noted above, Ga edge data on δ-Pu indicates even less damage produced, possibly indicating a role for Ga in maintaining the δ-phase even after self-irradiation. In particular, the main effect is determined to be due to gallium’s effect on the annealing rate, rather than on the damage production rate. In addition to these time/dose-dependent results, the δ-Pu sample that was stored for two months below 30 K was warmed while measuring the EXAFS, and a correspondence was observed between the isochronal annealing data in Figure 3(a), with a somewhat stronger correspondence with the magnetic susceptibility curves than the resistivity curves.

Most recently, Olive et al. [93] performed isochronal annealing EXAFS measurements on the same δ-Pu sample measured in Ref. [86], and introduced an analysis of particle size based on a method used in nanoparticles [94,95]. This method models part of the reduction in the EXAFS amplitude with dose as

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**Figure 5.** (a) EXAFS data on a single sample of PuCoGa$_5$ measured over the course of 3 years from Ref. [88]. (b) Total damage fraction from Pu L$_{III}$-edge EXAFS for PuCoGa$_5$ (purple squares), PuAl$_2$ (red triangles), and δ-Pu (inverted green triangles) that were stored at room temperature, together with Pu L$_{III}$-edge (filled magenta star) and Ga K-edge (open magenta star) data from δ-Pu stored below 30 K. Notes: (b) The lines show equilibrium models accounting for all the data with a single damage production rate and varying annealing rates [86].
Figure 6. Results of two different fitting methods for quantifying radiation damage in an isochronal annealing experiment. The first is an EXAFS fitting (EF) method that simply looks at the results of a shell fit, and the second uses a spherical crystallite (SC) model.

Notes: (a) Isochronal annealing results for EXAFS data collected at 15 K on $\delta$-Pu. The damage fraction is estimated from the overall amplitude reduction in a shell fit to the EXAFS data, and the changes in Debye–Waller factor, $\Delta \sigma^2$, and nearest-neighbor pair distance, $\Delta R$, are relative to the 300 K annealed data. (b) The same data fit to a particle size model with only the crystalline (undamaged) mean particle radius and the crystalline fraction as fitting parameters. Both figures are from Ref. [93].

due to the decreasing average size of the undamaged/crystalline portion of the material, providing a quantitative step forward in the ability for EXAFS to provide measurements of useful parameters in radiation damage studies. In this work, one obtains the $\delta$-Pu crystalline fraction, $F_C$, together with the mean crystalline particle radius, $R_C$, and is an improvement on the previous measurements in that the Olive et al. work accounts properly for this surface-to-volume effect. Together with the isochronal measurements which allow temperature-dependent broadening differences to be eliminated by always measuring the sample at the same temperature, clear features are elucidated in the EXAFS that correspond to the main features in both the resistivity and the magnetic susceptibility curves in Figure 3(a), as well as to the conjectures of Conradson et al. regarding the effect of local Ga ordering on the EXAFS data. Detailed shell fits to the isochronal EXAFS data, similar to some performed on PuCoGa$_5$ [88], show that small distortions occur around Ga at low annealing temperatures such that the disorder is better described as a mixture of more modest enhancements to the Debye–Waller factors, $\sigma^2$, than an overall amplitude reduction.
Changes in both the Debye–Waller factors and the nearest-neighbor bond lengths take place mostly in Stage II (see Figure 3(a)), and are virtually complete by Stage III. However, an interesting increase in the Ga–Pu $\sigma^2$ occurs near the end of Stage I and at the beginning of Stage II. This increase strongly implies that the lowest-temperature anneals are less disordered in Stage I than in Stage II, strongly suggesting that the Ga interstitials form a local phase in small crystallites until such temperatures that they become mobile, diffusing into more disordered regions. In other words, the Ga melts into the larger portion of the material, which has been effectively amorphized. The results of the particle size analysis shown in Figure 6(b) clarify this situation further, with the average crystalline particle size changing only slowly through temperatures as high as 200 K. Meanwhile, the crystalline fraction approaches unity from the Ga K-edge data at low temperature anneals, only dropping to fractions similar to the Pu L$_{III}$-edge values beyond 50 K.

These results are in strong agreement with the previous works mentioned above, and in particular with the idea, discussed in Section 2 that more covalently bonded materials will form local order in spite of the high degree of average disorder in a material (see Ref. [38,39]). Although the Ga ordering effect is clearest below 50 K, it supports the notion that such effects can occur at room temperature and affect quantities such as the lack of concentration dependence on the Ga–Pu bond length [19,76] and the considerations around the large local strain [75].

5. Conclusions

Although local structure measurements of radiation damage in Pu metals have occurred since the 1990s and have grown out of an older literature on such studies of radiation damage in general since the late 1960s, the field remains young due to the scant number of such studies and the many challenges faced in understanding this remarkably complex phenomenon. In this review, we have highlighted three major factors that must be isolated in order to obtain a clear picture of the effects of radiation damage: annealing, sample morphology (and, in some cases, history), and details of lattice distortions even relatively far from defects. From the very first experiments on metamict materials to understanding such behavior in elemental Pu, sample morphology and the competition between annealing and damage production have plagued progress in this field. Further experimental progress requires more isochronal data on other Pu materials, such as oxides and $\alpha$-Pu in order to fully understand the differing roles of ionic and covalent bonding. With the recent recognition of these issues, real tests of theoretical simulations are becoming possible, which will drive future progress in this field, ultimately leading, hopefully, to direct comparisons of calculated and measured RDF in Pu materials, such as those that have been made in other fields, e.g. ionic liquids [41].
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