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An Internal LLNL Report: Spectroscopic Signature of Aging in α -Pu(Ga)

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Abstract

Resonant Photoemission, a variant of Photoelectron Spectroscopy, has been demonstrated to have sensitivity to aging of Pu samples. The spectroscopic results are correlated with resistivity measurements and are shown to be the fingerprint of mesoscopic or nanoscale internal damage in the Pu physical structure. This means that a spectroscopic signature of internal damage due to aging in Pu has been established.

Introduction

Scientifically, the actinides remain an unresolved subset of condensed matter physics and chemistry. The physical and electronic structures of the actinides and actinide compounds have been the subject of many important and sophisticated investigations in the recent past. [1-15] Technologically, the issue of aging is of immense significance with long term impact on public policy. [16]

Previously, we reported the observation of strong age-dependent effects in the resonant photoelectron spectroscopy (RESPES) of Pu [17], but were unable to explain these observations. RESPES is a type of photoelectron emission in which additional emission channels are accessed along with the usual direct channel of photoemission. These additional channels are associated with core level excitations and a type of Auger-like decay. It was found that the RESPES effect was AMPLIFIED in an aged α -Pu(Ga) sample, instead of diminished as one might expect. So, once again, Pu has exhibited a counter-intuitive effect, but this time it appears to be associated with the Pu aging process. Examples of this are shown in Figure 1 below. In this report, we will demonstrate that these spectroscopic observations can be directly correlated with nanoscale disruptions of the mesoscopic ordering the Pu (Ga) physical structure.

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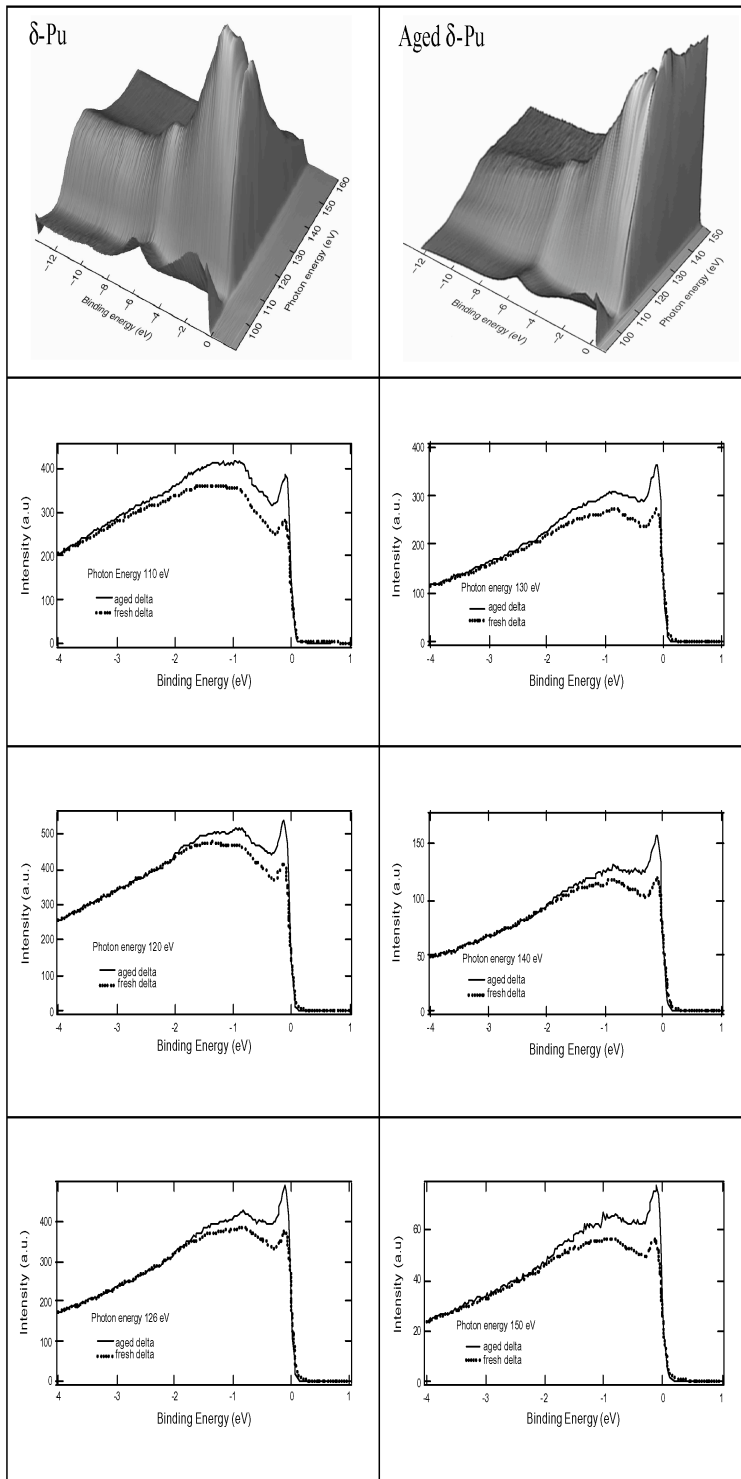


Figure 1. The RESPEC results for a new, highly purified δ -Pu(Ga) sample are compared with the corresponding measurements of an aged δ -Pu(Ga), that is approximately 10 years old. In the topmost panels are the pseudo-three dimensional plots, with binding energy (0 to -12 eV) and photon energy (100 to 150 or 160 eV) as the in plane axes and the out of plane axis being intensity. Here, normalization is via flux measurements using a gold grid up-stream from the photoemission site. In the lower panels, comparison of the new and aged samples is made at specific photon energies, over the resonance regime photon energy range. In these lower panels, normalization is made at points above the Fermi Energy and at a binding energy of 4 eV.

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Experimental

δ -Pu is stabilized at room temperature by the addition of a small amount of Ga or other dopants. [15] Details of the photoelectron spectroscopy [17], low temperature resistivity [18], dilatometry [19] and room temperature resistivity [20] experiments can each be found in its individually specified reference. Pu is highly radioactive and chemically toxic, so extreme care is required.

Discussion

The conventional wisdom concerning the spectroscopy of aging in Pu was that it was difficult, if not impossible, to observe age dependent effects. An example of this is shown below in Figure 2a. Here, the X-ray Absorption Spectroscopy (XAS) of aged and new delta Pu are almost identical.

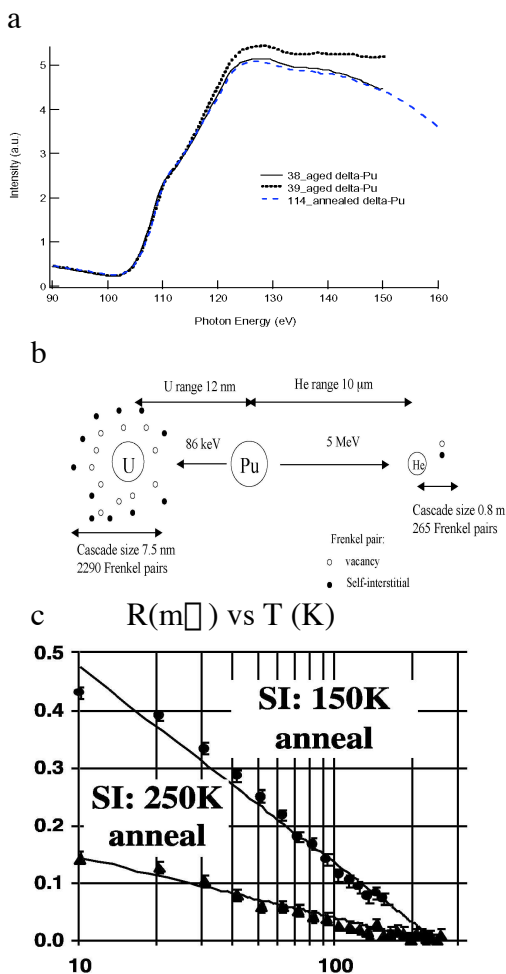


Figure 2

a) The XAS of new and aged δ -Pu(Ga) are shown here. Spectral scaling was made at the first edge, 100 –110 eV. Although there is a small vertical offset in one of the aged spectra, the overall appearance of the spectra are essentially the same. Thus it is unclear whether the spectroscopic difference in the XAS is meaningful or merely an artifact of imperfect normalization of beamline effects such as beam decay and beam shift.

b) This is a schematic of a possible Pu radiative decay, courtesy of W.G. Wolfer. The Pu atom emits an alpha particle, leaving behind a U atom. Both the alpha particle (He⁺²) and the U atom impinge upon the nearby Pu lattice.

c) An example of low-temperature resistivity measurements in self-irradiated (SI) Pu samples. Two measurements are shown: the upper with a pre-anneal of 150K and the lower with a pre-anneal of 250K.

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Thus, the XAS spectral data for new and aged α -Pu(Ga) do not exhibit any incontrovertible evidence of aging related effects. Similar results have been found for other spectroscopies. For example, Electron Energy Loss measurements of the 4d to 5f transitions in new and aged α -Pu(Ga) produce spectra which are essentially identical with that measured for α -Pu [14], within an uncertainty associated with the background subtraction. [21] Correspondingly, the wide PES scans of new and aged α -Pu(Ga) are very similar. [17]

Considering what is going on in the radioactive decay process, this absence of strong, undeniable spectroscopic indications of aging is somewhat surprising. As shown in Figure 2b, the emission of an alpha particle (He^{+2}) also induces a recoil motion in the newly generated U atom. Both of these processes will produce cascades of damage. Moreover, this type of damage from the alpha decay and other processes can be measured in what is essentially real-time via low temperature resistivity measurements, as recently illustrated by M. Fluss et al. [18] In Figure 2c, self-irradiated Pu samples exhibit resistivities that drop with increasing temperatures. This can be seen in both the negative slopes of the resistivity plots versus T(K) and in the initial values of each plot, which diminishes with the temperature of the pre-anneal.

Thus we return to a consideration of Figure 1. Here, there are strong indications of an aging-driven effect, independent of the normalization scheme. In the topmost panels, there is a comparison between the new and aged α -Pu(Ga) of the overall RESPES spectral result of each sample, using a cross normalization between individual photoemission scans based upon the photon beam intensity measurements made via an upstream gold grid. Each exhibits the sigmoidal shape of RESPES: the pre-resonance at 90 eV photon energy, the minimum of the anti-resonance at 100 eV photon energy and the high intensity of the resonance, starting at a photon energy of about 120 eV. The aged sample appears to have a much more extended resonance range, with a high intensity at the Fermi Level extending out to photon energies of 150 eV, while the new

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sample has a significant drop off as the photon energy moves through 140 eV , up to 160 eV. One could again raise the issue of normalization: perhaps the problem illustrated by the XAS results is also occurring here. As a test of that, an alternate normalization approach was used, where individual spectra at a specific photon energy, one each from the new and aged δ -Pu(Ga), were compared. Examples of this at photon energies of 110, 120, 126, 130, 140 and 150 are shown in the lower panels of Figure 1. Here, the pairs of spectra were normalized at energies above the Fermi Level and at a binding energy of -4 eV. It is possible to see that throughout the energy range, there is a consistent AMPLIFICATION of the intensity in the aged sample, on the scale 30% or so at the Fermi Energy. (The Fermi Energy is at a binding energy of 0 eV.) Changing the lower normalization energy from -4 eV to more negative values produced essentially the same result, although the exact magnitude of the spectral differences was dependent upon the normalization energy chosen.

Obviously, the next question is “why.” What is driving the differences in the resonant behavior? Logically, it must be some sort of extra-atomic effect. One possibility was MARPES, or multi-atom resonant photoemission. However, there are two problems with that interpretation: (1) the amplification effect is in the wrong direction (the amplification should be for the new, not the aged sample) and (2) earlier reports of large MARPES effects have been discredited and only much smaller effects are now asserted. [22] Alternatively, there has been a fairly recent report by Dowben of a different sort of extra-atomic effect in RESPES. [23]

Using the manganite system $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ or LCMO, Dowben showed that moving from a metallic phase at low temperature to a non-metallic phase at high temperature induced a very large increase in the resonant photoemission of the LCMO. He was able to explain this in terms of extra-atomic screening.[23,24] As shown in Figure 3a, if only intra-atomic decay is allowed, then there is only one possible decay process. However, if extra-atomic decay is allowed, then there are additional channels for decay. Dowben argued that in the localized

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case (non-metallic) the single decay channel allowed for the continued existence of the resonant behavior, but in the screened case (metallic), the extra atomic decay channels quenched the resonant effect. This is essentially what has been observed in Pu: the highly ordered new samples have superior screening, giving rise to a quenching relative to the aged samples. Because of the mesoscopic disorder in the aged samples, the extra-atomic screening is compromised, allowing the resonant behavior to be amplified relative to the new samples. To summarize: Increased screening quenches the RESPES, radiological damage restricts the screening in the aged sample and thus the aged sample has more RESPES.

Furthermore, it is clear that the underlying physics of the screening process and conductivity (the inverse of resistivity) would be the same. Diminished screening should thus correspond to diminished conductivity and greater resistance. Hence, it should be possible to test this hypothesis using resistivity measurements. However, the resistivity effects in room-temperature samples are different than the type of resistivity effects observed at very low temperatures, as shown in Figure 2c. At room temperature, many of the sources of the low temperature effects, e.g He bubble accumulation, may have been eliminated by an effective annealing at room temperature. Nevertheless, there has been strong evidence of aging effects in room temperature samples. For example, consider Figure 2b, where accelerated aging samples clearly show increases in length with time and hence dosage. Thus, although these samples have been at or near room temperature, the samples are experiencing aging affects.

The affect of annealing a room temperature sample is shown in Figure 3c. As the temperature is increased, from 120°C to almost 300°C, the relative resistance drops from 97% to 83%. A subsequent cooling to 30°C does not result in a reversal of the resistivity drop but rather causes only a small increase of a few %. Clearly, by performing this anneal up to over 300°C (573K), the nanoscale damage of the aged sample has been removed or at least reduced.

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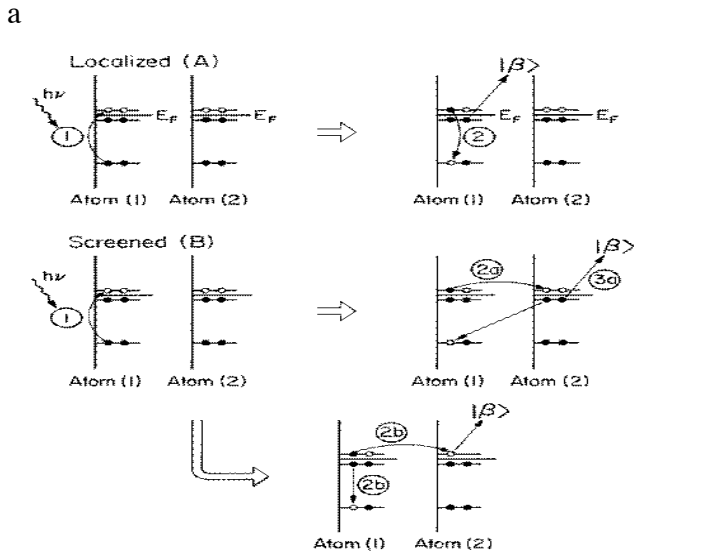
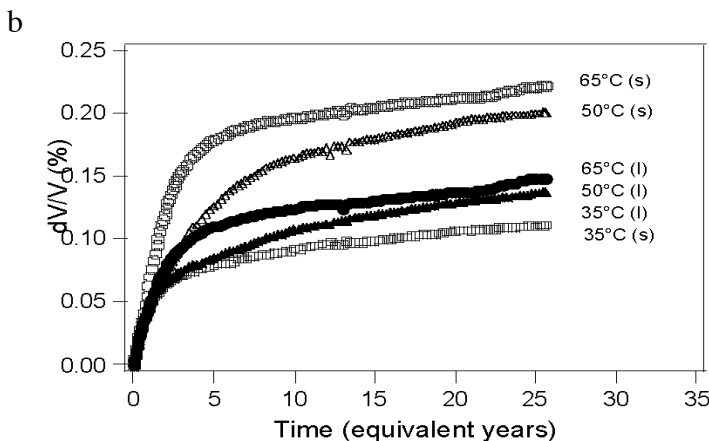
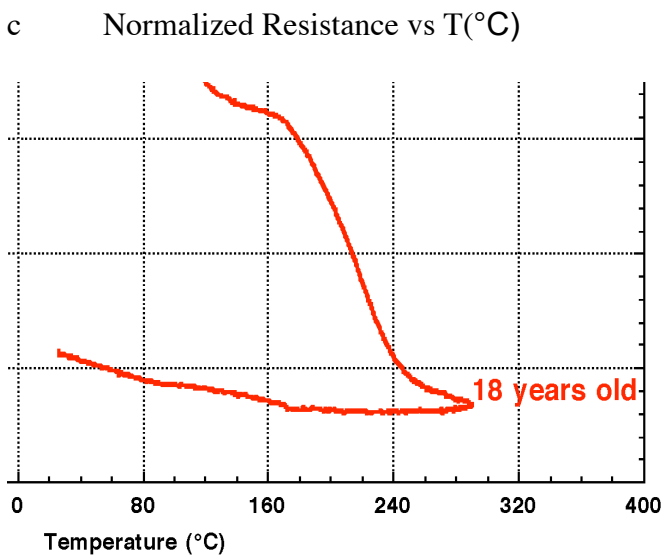


Figure 3

a) Intra- and extra-atomic channels of decay in the resonant photoemission process. Taken from Dowben [22].



b) Here is shown the sample length expansion of δ -Pu(Ga) with aging at room temperature. [19] In this case, accelerated aging was achieved by doping a Pu239 sample with 7.5 weight % of Pu238. The time equivalent in regular years is shown as the x-axis.



c) Normalized Resistance vs $T(^{\circ}\text{C})$: The effect of annealing upon the normalized resistance of room temperature δ -Pu(Ga) is shown here. Initially, the sample is warmed from 120°C ($R = 97\%$) to 280°C ($R = 83\%$) and then cooled to about 30°C ($R = 86\%$). This sample was 18 years old.

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Finally, it is worthwhile to consider the chemical impact of doping from the decay products in the Pu samples. As the various nuclear reactions occur, daughter elements will arise from the decay of the Pu sample. For example, in the alpha decay shown in Figure 2b, U daughter atoms will appear. However, based upon the known half-lives, it is estimated that after 10 years, less than 0.0034 % (atomic) of U will be produced in these Pu samples. Thus the concentration ratio of $[U]/[Pu] < 10^{-4}$. Hence it seems fairly unlikely that the mere presence of the dopants is sufficient to generate such effects as the RESPES amplification and resistance increase, but rather the mesoscopic scale damage caused by radioactive decay is the cause.

Conclusions

It has been shown that the amplified RESPES response in an aged Pu sample is due to the nanoscale damage of the aged sample. This analysis is founded upon a model of screening developed and experimentally tested independently by Peter Dowben. Furthermore, the model's application to Pu was tested via resistivity measurements versus temperature of a room temperature sample of Pu. We now have a spectroscopic signature of aging in Pu.

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