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S.K. McCall, M.J. Fluss, B.W. Chung, R.G. Haire

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Influence of radiation damage and isochronal annealing on the magnetic susceptibility of $Pu_{1-x}Am_x$ alloys

S.K. McCall[1], M.J. Fluss[1], B.W. Chung[1], and R.G. Haire[2]
[1]*Lawrence Livermore National Laboratory, Livermore CA 94550*
[2]*Oak Ridge National Laboratory, Oak Ridge TN 37830*

Results of radiation damage in Pu and $Pu_{1-x}Am_x$ alloys studied with magnetic susceptibility, $\chi(T)$, and resistivity are presented. Damage accumulated at low temperatures increases $\chi(T)$ for all measured alloys, with the trend generally enhanced as the lattice expands. There is a trend towards saturation observable in the damage induced magnetic susceptibility data. that is not evident in similar damage induced resistivity data taken on the same specimen. A comparison of isochronal annealing curves measured by both resistivity and magnetic susceptibility on a 4.3at% Ga stabilized δ-Pu specimen show that Stage I annealing, where interstitials begin to move, is largely transparent to the magnetic measurement. This indicates that interstitials have little impact on the damage induced increase in the magnetic susceptibility. The isochronal annealing curves of the $Pu_{1-x}Am_x$ alloys do not show distinct annealing stages as expected for alloys. However, samples near 20% Am concentration show an unexpected increase in magnetization beginning when specimens are annealed to 35K. This behavior is also reflected in a time dependent increase in the magnetic susceptibility of damaged specimens indicative of first order kinetics. These results suggest there may be a metastable phase induced by radiation damage and annealing in $Pu_{1-x}Am_x$ alloys.

Introduction

Plutonium and its simple binary alloys are known to be extremely sensitive to impurities, defects, and particularly disorder. One interesting method of adding disorder is to alloy plutonium with americium, $Pu_{1-x}Am_x$, forming a stable fcc phase (δ-Pu, β-Am) from $0.06 < x < 0.80$ where the lattice parameter increases with x. The electronic structure of americium is $5f^6$, thus it has a J=0 ground state and its magnetic susceptibility is primarily due to a large Van Vleck contribution[1]. Being a single ion effect this should be independent of the local environment and thus should be insensitive to radiation damage. Thus any changes observed in the magnetic susceptibility of the PuAm alloys that deviate from a simple linear combination of the two end members should reflect a change in the magnetic properties of the plutonium.

Another method for adding disorder is through the radioactive decay of Pu and Am which produces a ~5 MeV α-particle and a corresponding recoil (U or Np) that creates a large number of vacancies and interstitials, of which a substantial fraction, after relaxation, remain frozen in place at low temperatures. Disorder from self-damage increases with time and is observable through magnetic susceptibility measurements, where Curie Weiss behavior evolves and thus demonstrates the creation of local magnetic moments. These emergent moments may be removed by thermal annealing, proving they arise from the disorder created by vacancies and interstitials. Radiation damage studies

on $Pu_{1-x}Am_x$ alloys thus allow investigation of how inherent chemical disorder and structural disorder each influence the behavior of the electronic structure of plutonium.

Radiation Damage

Plutonium-239, with a half-life of 24,110 years, radioactively decays by emission of a 5.04 MeV α-particle and corresponding 85.8 keV U recoil, which produces numerous Frenkel pairs (a vacancy and interstitial).. The α-particle travels ~10 μm losing most of its energy through electronic excitations and ionization of Pu atoms, creating only a relatively few Frenkel pairs near the end of its range. On the other hand, the U recoil and resulting atomic collisions is expected to be contained within a volume on the order of 10 nm across. Contained within this volume is an instantaneously generated dense cascade of several thousand vacancies and interstitials, the majority of which are expected to recombine as the lattice rapidly cools, leaving only a few hundred defects. Recent molecular dynamics simulations[2] find the extent of the U-recoil damage cascade may be significantly larger than earlier predictions. These observations may be consistent with recent experimental work[3] that, based on bulk magnetic measurements, finds each α-decay affects on the order of half a million atoms for both α-Pu and gallium stabilized δ-Pu. Alloys of $Pu_{1-x}Am_x$ produced with ^{243}Am also form the delta phase of plutonium where the lattice parameter expands with increasing americium concentration. The ^{243}Am has a half-life of 7,370 years, making it more than three times as active as ^{239}Pu. It decays by emission of a 5.27 MeV α-particle and a corresponding 87.4 keV Np recoil, which then decays by β-emission with a half-life of 2.9 days to ^{239}Pu. The recoiling Np ion is comparable in energy to the U recoil resulting from the Pu decay, while the β-emission imparts a recoil of less than 1 eV on the resulting Pu ion. While molecular dynamics simulations have not been done on PuAm alloys, the resulting damage cascades do approximate those of δ-Pu.

Magnetic Susceptibility

The magnetic susceptibility of pure α-Pu has a large temperature independent contribution of $\sim 5.1 \times 10^{-4}$ emu/mol indicative of a narrow band at the Fermi level, which is consistent with the large electronic density of states reported from specific heat measurements[4]. For δ-Pu, stabilized by few atomic percent Ga it is substantially equivalent to the α-Pu phase, while for somewhat larger concentrations of Am, the magnetic susceptibility is roughly 40% larger than observed in α-Pu and shows weak temperature dependence, but does not display any indication of significant local moments beyond a weak Curie tail expected from impurities at the level of a few hundred ppm or less. As the lattice in the delta phase is further expanded by inclusion of Am, the magnetic susceptibility also increases, and a weak temperature dependence develops at higher temperatures reminiscent of spin fluctuations observed in intermetallics such as UAl_2[5]. However, when these alloys are permitted to accumulate damage at low temperatures where the damage cascade remnants are frozen in place, a temperature dependent contribution to the magnetic susceptibility evolves that fits well to Curie-Weiss behavior. Damage accumulation at the level of a few α-decays per million atoms

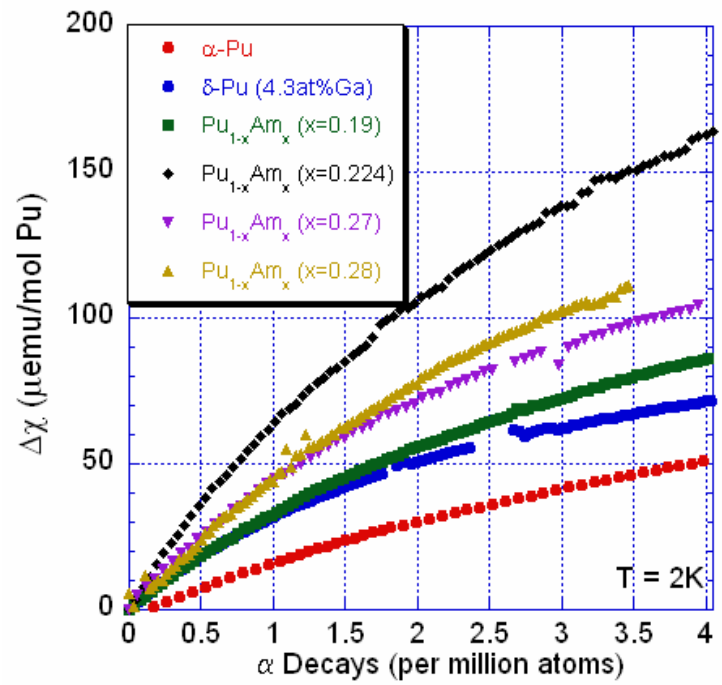

Fig. 1 Increase in magnetic susceptibility per mol Pu due to self damage accumulated at low temperatures. Apart from the 22.4% Am specimen, the effect increases with increasing lattice constant. The curvature as a function of damage suggests this effect is saturating.

equates to periods of about a month and result in a contribution that is still significantly smaller than that of the undamaged specimens, but is appreciable when considered in relation to the number of alpha decays. The magnetic susceptibility resulting from the accumulated damage shows signs of saturating as indicated in Fig. 1 where the increase in magnetic susceptibility as a function of the number of α-decays is shown for 2K isotherms across a series of Pu and PuAm alloys. With the exception of the 22.4% Am sample, the damage induced change in susceptibility monotonically increases with increasing lattice parameter. This is not surprising given that an expanded lattice will more easily accommodate vacancies and interstitials indicating a lower displacement energy threshold. The self-damage induced increase in the magnetic susceptibility displays strong temperature dependence for all specimens measured thus far. In the dilute case, the damage induced contribution fits well to a modified Curie-Weiss law which is indicative of local moments. Such a result would not be all that surprising were the underlying plutonium magnetic. That these moments develop in a system with no indication of local moments[6] is quite remarkable and implies this accumulating disorder provides an observational window into the heretofore hidden nature of the 5*f* electrons, effectively driving them toward a more localized state.

Isochronal Annealing

The majority of vacancy and interstitial pairs created from self-irradiation damage recombine in the following nanoseconds before the lattice returns to thermal equilibrium. At sufficiently low temperatures, the remaining defects will be frozen in place. These defects can be removed through thermal annealing, with self-interstitials becoming mobile at lower temperatures than vacancies. The temperatures at which the defects are annealed away can be mapped by the process of isochronal annealing. In this process, after radiation damage is accumulated for a period of time, a property that changes as a function of accumulated damage is measured repeatedly at a fixed temperature. Between each measurement, the sample is rapidly warmed to an annealing temperature, soaked for a fixed period of time, and returned to the measurement temperature. In the ideal case,

the transition between the measuring and annealing temperature is instantaneous. As the radiation damage is annealed away, the measured property should monotonically return to the value it had in the undamaged state. A more detailed description of this technique can be found elsewhere[7, 8]. For many metals and compounds, distinct features can be identified through examination of a plot of the fraction of damage retained as a function of the annealing temperature, and these define distinct annealing phases.

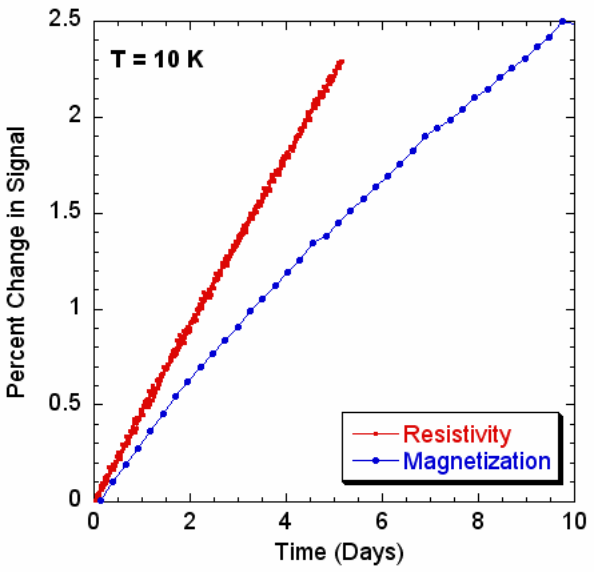

Fig. 2 Damage accumulation in δ-Pu(4.3at%Ga) as a function of time as measured by 2 different techniques on the same sample.

The manner in which radiation damage alters physical properties varies with the property measured. A simple illustration of this is shown in Fig. 2, where the fractional change as a function of time (damage) is shown on the same sample for two different measurement techniques: resistivity and magnetization (magnetic susceptibility). Here, the magnetization was measured on a small sample of δ-Pu(4.3at%Ga) in a 3T magnetic field at 5 K, the details of which have been previously described[9]. This specimen was then melted, and rolled into a 75 μm thick foil, on which the resistivity was measured using the Van der Pauw technique[10]. Several differences appear in this figure. Most obvious, is that the rate of change differs for the two properties, with the resistivity increasing more rapidly than the magnetization. Secondly, there is a distinct curvature that develops in the magnetization measurement that is not reflected in the resistivity measurement. Since magnetization is a bulk measurement, this curvature has been used to estimate the size of the radiation damage cascade's influence on the induced magnetization. Resistivity is a transport measurement, and thus path dependant, so simple models predicting the volume influenced are not applicable. Other groups have observed a developing curvature in

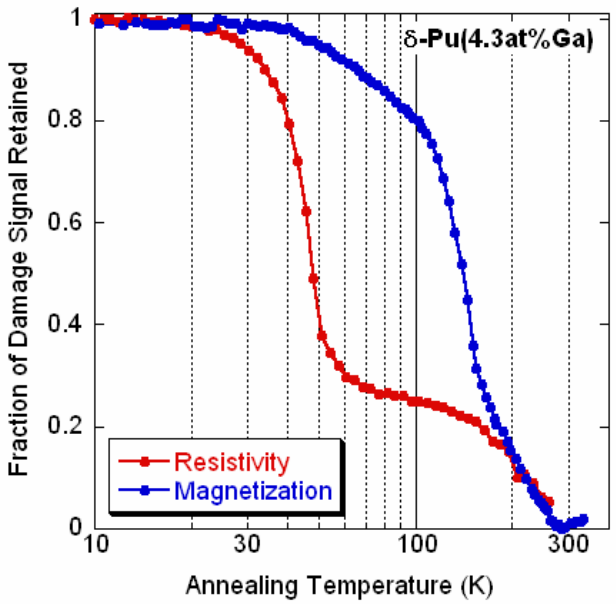

Fig. 3 Isochronal annealing as measured by resistivity and magnetization on the same sample. Stage I annealing, as represented by the steep drop in the resistivity curve, is missing in the magnetization curve. This suggests that magnetization is relatively insensitive to interstitials.

resistivity over much longer time scales on the order of hundreds of days[11].

Some measurements will be more sensitive to a specific type of defect than others, so the fraction of damage retained is an artificial construct that can not presuppose the measurement is equally sensitive to each type of defect. Thus the correct way to describe the ordinate axis in an isochronal annealing curve is the fraction of the damage *signal* retained, not the fraction of damage. The physical property used to monitor the annealing process may show a different sensitivity to different types of radiation damage. This is shown in Fig. 3 for Ga stabilized δ-Pu, where there is a dramatic decrease in the resistivity isochronal annealing curve at Stage I, where interstitials begin to move, but very little change was observed in the corresponding magnetic susceptibility isochronal annealing curve. There was a caveat in the earlier work, because the magnetic susceptibility data was obtained on a δ-Pu specimen stabilized with 4.3 atomic percent Ga, which was compared with resistivity measurements on a 3 atomic percent Ga specimen. Resistivity isochronal annealing measurements have now been completed on the same δ-Pu(4.3at%Ga) specimen used for the magnetic susceptibility results, as shown in Fig. 2, and the results are consistent with the prior work on 3at% Ga. This confirms the prior assertion that in the case of δ-Pu, interstitials have little influence on the magnetic susceptibility.

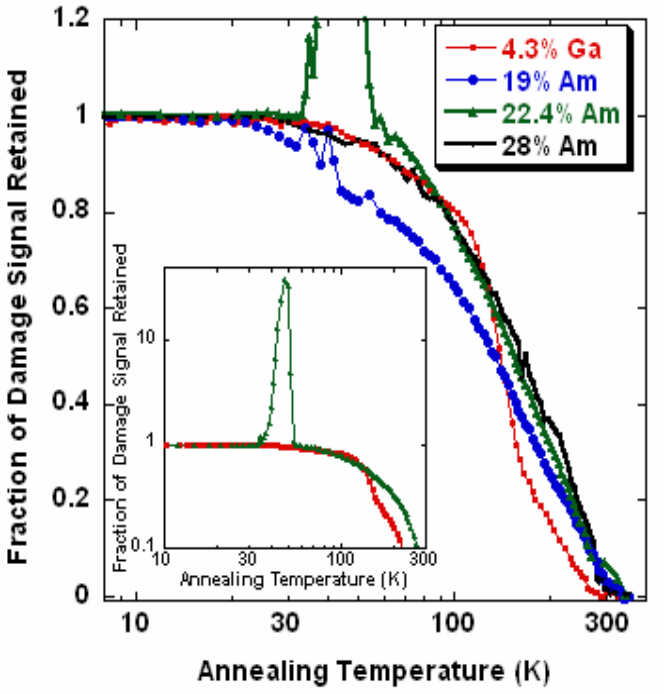

Fig. 4 Isochronal annealing curves for delta phase Pu specimens. The distinct features of the 4.3at% Ga stabilized phase are smeared out in the $Pu_{1-x}Am_x$ alloys. The 22.4% Am alloy shows a remarkable increase in magnetization near Stage I, that is more clearly illustrated on a log scale in the inset. Similar but less dramatic features are observed in the 19% Am alloy. This "reverse annealing" may be indicative of a damage

In alloys, as opposed to intermetallic compounds, the distinct phases of annealing may be smeared out due to the disorder inherent in the system. This is shown in Fig. 4 where the distinct stages observed in the Ga-stabilized δ-Pu are no longer readily extracted from the PuAm alloy curves. A second feature, abundantly clear in the 22.4% Am specimen is an anomalous increase in the signal retained with increasing temperature, where the signal grows to ~40X the initial damage signal near the temperature where Stage I annealing takes place in other alloys. This is illustrated in the inset of Fig. 4, where the "fraction of damage signal retained is shown on a log-log plot along with the Ga-stabilized Pu specimen. The 19% Am curve shows a similar tendency beginning at roughly the same temperature, although it is much less dramatic. In the simple picture of annealing out damage, the curve should monotonically decrease for each higher temperature since less damage is

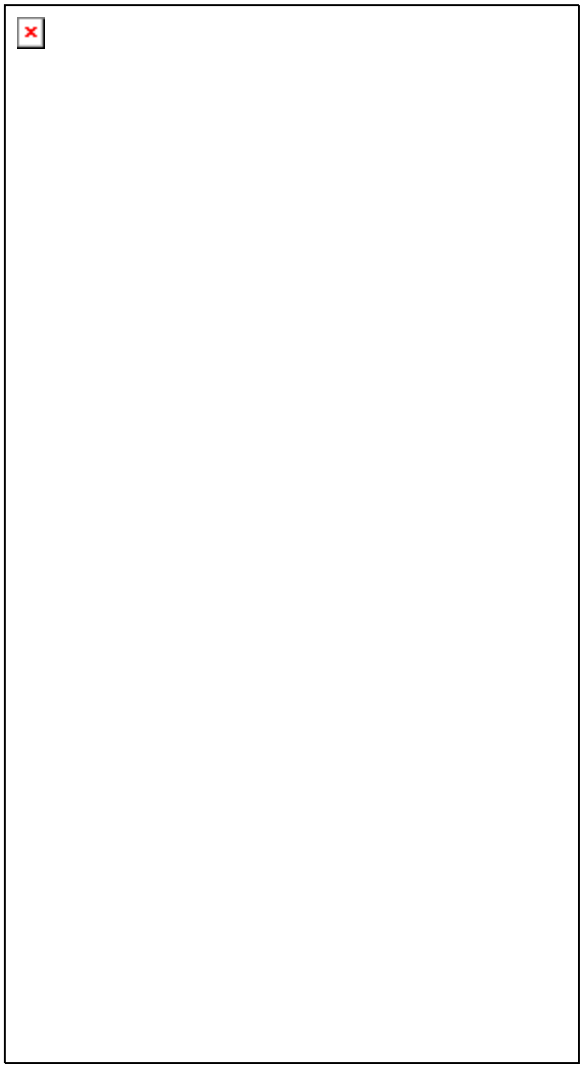

Fig. 5 Magnetic susceptibility of $Pu_{(1-x)}Am_x$ (x=0.19) after accumulating damage at low temperatures (red) and after annealing at 350K. (blue) following the same protocol. The lower figure shows the time dependence of the 44K isotherm in the upper figure. The fit indicates 1st order kinetics.

retained after successive anneals. Small increases in annealing curves have been observed previously[12] for several other alloys such as Cu_3Au, where the increase in signal was termed "reverse annealing". One explanation for such behavior is that the radiation damage is either disordering an ordered intermetallic system, or creating small ordered regions in an otherwise disordered system.

All of the isochronal annealing curves are obtained from measurements at one fixed temperature. Some insight may be gained by looking at the behavior of the measured property at each of the annealing temperatures—essentially the other half of the measurement.. Fig. 5 shows this for the 19% Am alloy, where the upper figure shows the measured signal at progressively higher temperatures of both the damaged sample (red), and a repeated set of measurements following the precise annealing protocol with the same sample after annealing at 350K for several hours (blue). At each temperature, the specimen was soaked for a fixed period of time, and in between each of these soaks, the specimen was cooled to T=5K to generate the isochronal annealing curve shown in Fig. 4. There is a significant change in the damaged sample that manifests between 35K and 45K, where the magnetic susceptibility distinctly increases with temperature, as compared to the simpler behavior observed in the annealed specimen where no such increase is evident. The measured behavior is changing as a function of time at these temperatures, and that is reflected in "stacked" isothermal points of the damaged specimen. The 44K isotherm is shown as a function of time in the lower part of Fig. 5, where it fits well to a simple exponential, indicating this transition obeys first order kinetics. The fitting parameters are shown in Fig. 5, where the characteristic time of 5.36 minutes, which is roughly one half of the annealing soak time. This suggests that a shorter soak time might enhance the "reverse annealing" effect observed in the isochronal annealing curve shown in Fig. 4.

Conclusions

Self damage in plutonium and PuAm alloys increases the magnetic susceptibility, and the magnitude of the increase per α-decay generally increases with increasing lattice parameter. All of the magnetic measurements show a trend towards saturation at a defect concentration of only a few α-decays per million plutonium atoms, which is much more rapid than the trend observed in measurements such as resistivity, even when measured on the same sample, as reported here. Resistive and magnetic susceptibility isochronal annealing measurements on 4.3at% Ga stabilized δ-Pu show that "Stage I", the point at which interstitials begin to move, is largely not detected by the magnetic measurement. This implies that interstitials contribute little to the magnetic signature of self-damage.

The general features of individual isochronal annealing stages are largely smeared out in the alloys with a significant fraction of americium, which is not surprising for alloys as compared to intermetallic compounds. There is an unexpected increase in the signal from isochronal annealing with magnetic susceptibility observed in several alloys near 20% doping with Am that occurs near the temperature where interstitials begin to move in other δ-phase alloys. A preliminary examination of the magnetic susceptibility at these temperatures reflects an anomalous increase in the signal not observed in fully annealed specimens, or in damaged specimens at lower temperatures. This signal is time dependent, suggesting it reflects a kinetic process. The time dependence fits well to an exponential function indicating 1st order kinetics, and may reflect the presence of a damage induced metastable phase. New measurements on additional samples near this concentration are under way.

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