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Effects of self-irradiation on local crystal structure and $5f$ localization in $PuCoGa_5$

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X-ray absorption fine-structure (XAFS) measurements demonstrate the structural and electronic changes involved in destroying superconductivity in $PuCoGa_5$ due to self-irradiation damage. In particular, the Pu $L_{\rm III}$-edge data indicate a more localized f-orbital relative to the itinerant paramagnet $UCoGa_5$, potentially increasing with radiation damage. Moreover, the local crystal structure in aged material is disordered much more strongly than expected, consistent with all atoms within a damage cascade displaced from their equilibrium positions.

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The discovery of superconductivity at T_c=18.5 K in $PuCoGa_5$ [1] raises many fascinating questions about how a heavy-fermion superconductor can have a T_c nearly an order of magnitude higher than all other known examples. Although the layered nature of this material is thought to play a substantial role in analogy to the cuprates [2], the role of local $5f$ moments in forming the pairing state remains enigmatic. Moreover, lattice deformations are practically intrinsic to this material due to self-irradiation damage from the decay of the plutonium nuclei. Here, we report x-ray absorption fine-structure (XAFS) measurements that further demonstrate the localized character of the $5f$ orbital, and the surprisingly large effect of self-irradiation damage on both the local crystal structure and the degree of $5f$ localization [3].

Recent photoemission results demonstrate strong evidence for both localized and itinerant $5f$ character [4]. Such a "dual nature" of these magnetic orbitals would be unusual for what appears to be a moderately heavy-fermion material, with an electronic linear specific heat Sommerfeld coefficient $\gamma \approx 100$ mJ/mol K^2 and a normal state Curie-Weiss-like susceptibility consistent with local moment behavior [1]. Moreover, the radioactivity of plutonium generates damage cascades that are thought to be responsible for the high upper critical field $H_{c2} \approx 100$ T and critical current density $J_c > 10^4$ A/cm^2 for $T > 0.9T_c$, although these values remain high even in the freshest material. Clearly, self-irradiation damage plays an important role in these superconductors by reducing the coherence length and creating pinning centers, and may play a role in the local moment behavior as well. Most of the work describing the bulk properties of $PuCoGa_5$ as a function of radioactive decay has been performed by Jutier and co-workers [5, 6]. They have found, for instance, that T_c decreases by about 0.24 K per month, and that H_{c2} peaks ~ 120 T after about a year in samples with mostly ^{239}Pu [5]. Curro *et al.* [7] have found that the impurity scattering rate inferred from nuclear magnetic resonance experiments agrees well with the reduction in $T_{\rm C}$ an aged sample. Obtaining microscopic information about how this radiation-induced disorder evolves and contributes to these changes is therefore of fundamental importance toward understanding superconductivity in this exceptional material.

In this paper, we utilize the XAFS technique to provide local atomic species-specific pair-distance information [8]. Complementing the structural aspects, $L_{\rm III}$ absorption edge data are used to determine the degree of $4f$ electron localization. Although this technique has been less useful in light-actinide than in rare-earth intermetallic systems due to the more extended nature of their $5f$ orbitals, energy shifts and changes in line shape have been observed to correlate with the degree of $5f$ localization [9–12], and some of these observations have been reproduced in *ab initio* calculations [13]. Such effects may be enhanced in plutonium intermetallics due to the position of Pu at the transition between local and delocalized f electron behavior between the light and the heavy actinides [14].

Two $PuCoGa_5$ samples were synthesized [1]. At the time of the most recent x-ray measurement, one was 24.3 months old (Sample A), and the other was only 0.5 months old (Sample B). Sample B had a $T_{\rm C} = 18.1$ K when it was 3.1 months old, and Sample A had a $T_{\rm C} = 12.4$ when 27.4 months old. The isotopic content is the same for both samples with the main radioactivity coming from 93.93% ^{239}Pu, 5.85% ^{240}Pu, and 0.12% ^{241}Pu. This sample therefore has an α decay rate $\lambda_\alpha \approx 3.43\times10^{-5}$ per Pu per year. The accumulated dose has been shown to be a reasonable indicator of how sample properties change with time [6], and we report the sample age in units of α-decays per atom, which we refer to as f_α. We do not use the more common "displacements per atom" (dpa) unit, because it generally assumes the

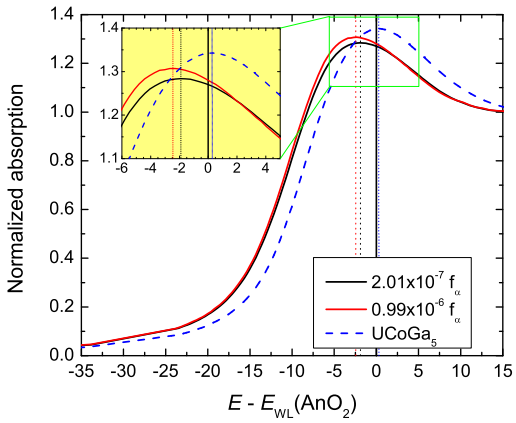

FIG. 1: Actinide $L_{\rm III}$-edge data comparing 115 samples to each other as a function of the shift of the main peak ("white line") energy, $E_{\rm WL}$ (vertical dashed lines), relative to the corresponding tetravalent actinide oxide, UO_2 or PuO_2 (solid line). The relative energy shifts are +0.30, -1.90 eV and -2.45 eV for $UCoGa_5$, fresh $PuCoGa_5$ and aged $PuCoGa_5$. $PuCoGa_5$ are given in units of α decays per atom, or f_α. The inset shows a zoom of the white line region.

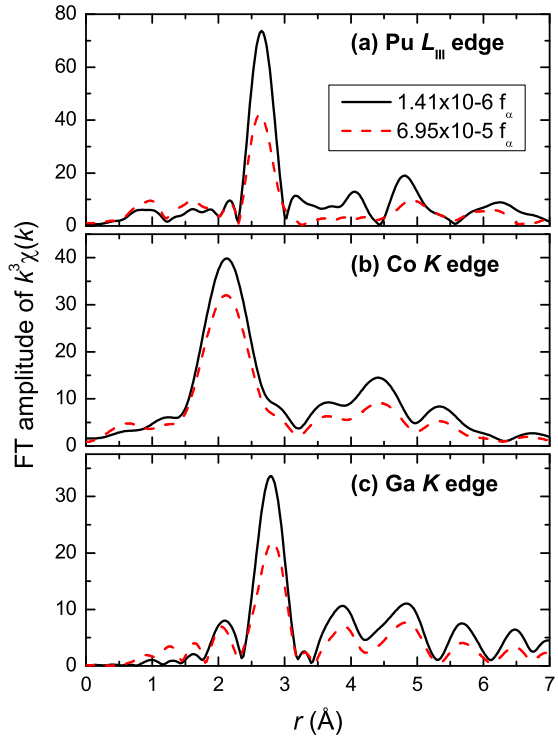

FIG. 2: FT of the $k^3\chi(k)$ EXAFS data from the (a) Pu $L_{\rm III}$, (b) Co K, and the (c) Ga K edges are shown for both a fresh and aged sample. Transform ranges are between 2.5-16.0 Å^{-1}, 2.5-10.0 Å^{-1}, and 2.5-15.0 Å^{-1}, respectively, all Gaussian broadened by 0.3 Å^{-1}.

number of displaced atoms (Frenkel pairs) is a known quantity from a Kinchin and Pease (KP) [15] or related model, and we show below that this model may not accurately reflect the actual number of displacements.

Figure 1 shows the U $L_{\rm III}$-edge data for $UCoGa_5$, an itinerant paramagnet [16]. The data are plotted as a function of energy relative to the position of the UO_2 white line, $E_{\rm WL}$. Comparisons between light-actinide metallic and oxide compounds have usually shown a strong similarity between the positions of the dioxide (tetravalent actinide) and metallic $L_{\rm III}$ absorption maxima ("white lines"), generally interpreted as due to the extended $5f$ orbital rather than a tetravalent (eg. $5f^2$ state in U) ground state in the metallic compounds [9–12]. This interpretation is supported both by *ab initio* calculations [13] and by experiments under applied pressure [12]. The observed small shift between the U $L_{\rm III}$ edge data for $UCoGa_5$ and UO_2 is consistent with the lack of significant shift in most other measured itinerant U-based intermetallics.

These data contrast with $PuCoGa_5$ data in Fig. 1 which show a significant shift for $PuCoGa_5$ versus PuO_2. Moreover, the shift is noticeably larger in the two year old material (-2.45 eV) compared to the fresh sample (-1.90 eV). For comparison, the energy shift between Pu(III) and Pu(IV) aquo ion is typically about -4.4 eV [17, 18], and the shift from itinerant to local $5f$ behavior in U compounds has been measured to be about -2 eV, both between different phases [9, 10] and under applied pressure [12]. Shifts as large as -6 eV have been observed between PuO_2 and several chalcogenides [11]. The present data therefore strongly suggest that the aged material has a more strongly localized f orbital than that in the fresh sample, which is still localized compared to that in $UCoGa_5$. We must stress, however, that structural effects can also cause shifts in the white line position. Because of the comparison to the $UCoGa_5$ sample, we believe the main portion of the shift is indeed due to f localization, however, we cannot rule out that the shift with sample age is due to radiation damage to the crystal structure. In any case, this result is not only significant because of the observation of local moment behavior, but also because it shows that such measurements are possible from Pu $L_{\rm III}$ edge XANES data from Pu intermetallics, further emphasizing the position of plutonium in the periodic table between local and delocal f-orbital states.

The Fourier transformed (FT) XAFS data from all three absorption edges for a fresh sample of $PuCoGa_5$ are shown in Fig. 2 [16]. The most reliable fits are to the Pu $L_{\rm III}$-edge data. Fits of the temperature dependence of the mean-squared displacements of the pair distances, σ^2, are well described by a correlated-Debye model [19] with no evidence of static disorder. All the measured pair distances agree well with diffraction results [16]. The Co

K-edge data support these results, but are limited to a shorter k-range, and various correlations between the fit parameters limit reliable results to the first peak. Although the quality is quite high for the Ga K-edge data, the multiple Ga sites complicate the fits and make results comparing different aged samples unreliable. However, for both the Co and Ga edge, there is no evidence of any unusual disorder in the fresh samples.

Figure 2 also shows FT data for an aged sample. Detailed fits show that the main difference between these data and those from the fresh sample is an overall amplitude reduction in the older sample. Such a difference indicates that some fraction of the aged sample is strongly disordered or distorted relative to the $PuCoGa_5$ crystal structure. The presence of such disorder is not surprising, since the recoiling U nucleus from the α decay of a Pu atom is expected to redistribute thousands of atoms [20], not unlike melting followed by a very fast quench. In the Pu and Co edge data, the fits show that both the overall scale factor S_0^2 decreases and the σ^2 value increases with age. This situation suggest that there are three distinct regions within the aged samples: virtually undamaged, strongly damaged, and mildly damaged. The latter region may exist, for instance, on the edges of strongly damaged regions. We therefore describe the total damaged fraction $f_{\rm tot}$ as due to the sum of the strongly damaged fraction $f_{\rm s}$ and the mildly damaged fraction $f_{\rm m}$. Since EXAFS amplitudes $A \sim 1/\sigma$, as long as $\sigma_{\rm m}$ is large enough, $f_{\rm tot} \approx S_0^{2\prime}(t)/S_0^2(0)$, where $S_0^{2\prime}(t)$ is obtained from fits where $\sigma^2(t)$ are fixed at $\sigma^2(0)$. Without reliable fits for the Ga edge data, we instead estimate $f_{\rm tot}$ by using the amplitude ratios of the main EXAFS peak. This simplification yields similar results for the Pu and Co edges [3]. Results for $f_{\rm tot}$ are shown in Fig. 3.

The Pu edge data are of sufficient quality that we can use this estimate of $f_{\rm tot}$ to obtain $f_{\rm m}$ by performing a fit where the $\sigma_2(t)$'s are no longer constrained, in which case $f_{\rm s} \approx (S_0^2(t) - S_0^{2\prime}(t))/S_0^2(0)$. Correlations between the S_0^2 and σ^2 parameters are more difficult to control in such a procedure, but we find that $f_{\rm s} \approx 0.2$ and $\sigma_{\rm m} \approx 0.0055$ Å^2 for all of the aged samples measured.

To give some perspective to these damage fractions, $f_{tot} \approx 25\%$ after one year corresponds to $N_{\rm D} = 7 f_{\rm tot}/\lambda_\alpha \approx 50,000$ atoms displaced per α decay. About 80% of these are in a strongly damaged state, that is, where the Debye-Waller factors are large enough or the atomic species and coordination numbers are variable enough that their local structure no longer contributes to the EXAFS signal.

Although a modern theoretical treatment of radiation damage in $PuCoGa_5$ is currently not available, we can base our analysis on work done on δ-Pu materials [21, 22]. In this model, the α-particle generated by the decay of a ^{239}Pu nucleus has about 5 MeV of energy and, using the KP model, generates nearly 300 Frenkel pairs over a distance of nearly a micron [20]. Most of the damage,

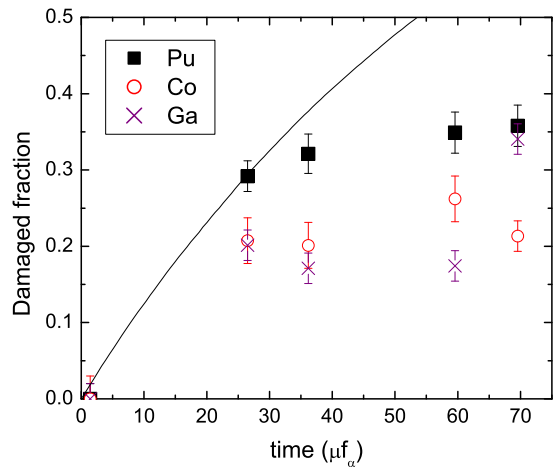

FIG. 3: Estimates of the total fraction of displaced atoms as a function of the number of α decays per atom (f_α), as seen from the perspective of each atomic species. Error bars are based on reproducibility. Absolute errors are about ±5%. The line shows percolation behavior based on the first Pu data point, demonstrating that damage is slower than expected from a strict overlap model.

however, is done by the recoiling ^{235}U nucleus with 86 keV, which produces nearly 2300 Frenkel pairs. These energetic particles create damage cascades that extend over nearly 10 nm, with a defect volume fraction of about 3%. Density functional theory can then determine the relaxed equilibrium positions of these defect atoms, such as has been done in volume-change calculations [21]. Intermediate time-scales have been explored with molecular dynamics and kinetic Monte Carlo techniques. These latter calculations show that the effective number of defects is reduced by as much as a factor of 10 within only a few picoseconds [22]. These values should not change substantially in $PuCoGa_5$, and in fact a rough TRIM code [23] calculation using default values generates similar damage rates and ranges within a KP model.

Using these models, we expect around 300 pair defects to survive the initial recombination, or 600 defects per α decay. Instead, we measure a much larger number, namely, 50,000 defects per α decay. This value is higher than the theoretical estimate even if one doesn't allow any lattice relaxation after defect formation. In fact, if one assumes a ~10 nm damage cascade as expected for δ-Pu, then *every* atom in the cascade has been displaced from its equilibrium position. One major reason for the discrepancy between the calculations and the measurement may be that only 1/7$^{\rm th}$ of the atoms are Pu. However, if this were the case, Ga atoms should show a much smaller damage rate, and although there is some evidence that their rate of damage is indeed smaller, it is not an order of magnitude smaller. Although this difference is

undoubtedly important, local lattice distortions must be playing the dominant role, with both distortions around defect sites and associated further neighbor distortions dominating the local structure.

Also shown in Fig. 3 is the prediction of a cubic percolation model of the overlap of damaged regions. The time axis is chosen such that the model agrees with the first Pu edge data point. Clearly, the damage does not proceed at as fast a rate as expected from the early data. This disagreement is very likely due to self-annealing effects [24] caused by the room-temperature storage of the samples between measurements. Since an interstitial defect should anneal more slowly than a simple distortion, the damage cascades will likely not be completely damaged after some time, but instead will have growing pockets of nearly ordered material surround by strongly damaged material. Although these pockets may be nearly ordered, they will not be superconducting until, at a minimum, they are larger than the coherence length ξ_0 which is estimated to be 2.1 nm [1]. This distance is already larger than the KP predicted distance between Frenkel defects. Therefore, we are more interested in the fraction of the material that exists within the volume defined by the edges of a damage cascade, which may well be better described by the percolation model depicted in Fig. 3. According to this extrapolation one might expect superconductivity to cease between 3.5 and 4 years for these samples. This simplification, of course, doesn't account for any proximity effect, which should increase this time period, or any increased impurity scattering, which would decrease this time.

The physical picture that is emerging is one where the recoiling U nucleus generates much more damage than expected based on models of elemental Pu. This damage is likely dominated by near-neighbor lattice distortions that extend into the second coordination sphere or beyond, possibly generating local distributions of impurity phases. This damage is so severe that it encompasses all the atoms in a given damage cascade. The effective damage rate is slowed as the material anneals at room temperature. The partially localized f electrons in the well-ordered material are apparently further localized in the damaged regions, probably creating non-superconducting material both due to the localization and strong defect scattering in these regions, although a proximity effect could still allow some superconductivity. Annealed areas within a damage cascade probably would not be superconducting due to their limited size, unless they reach the edge of a cascade.

These results underscore the need for more studies of radiation damage in this material. Only through better theoretical models and microscopic probes can we understand the detailed electronic and structural properties of damaged regions and how they couple to the superconductor. Improvements in these areas will have ramifications not only for understanding superconductivity in $PuCoGa_5$, but also to the field of radiation damage in general.

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