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Intrinsic Nanoscience of δ Pu–Ga Alloys: Local Structure and Speciation, Collective Behavior, Nanoscale Heterogeneity, and Aging Mechanisms

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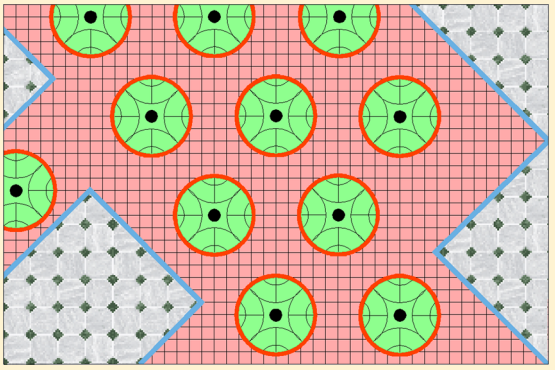
ABSTRACT: δ Pu–Ga alloys and their response to self-irradiation are important scientifically because of the unique complexity of Pu and technologically because of their importance in Science Based Stockpile Stewardship. The local order and structure and the role of the Ga are crucial to understanding the phase stability and the aging effects. X-ray diffraction that gives the long-range average structure of the periodic component of the materials and pair distribution functions analysis and X-ray absorption fine structure that give the overall and the element specific local structure have been used to examine a variety of new and aged materials, including a set of high purity δ $Pu_{1-x}Ga_x$ alloys with $1.7 \leq x \leq 6.4$ atom % Ga that span the low [Ga] portion of the δ region of the phase diagram across the ~3.3 atom % Ga metastability boundary, a ~1.7 atom % Ga alloy that was enriched with Pu^{238} to accelerate the aging process, and others. We find that metastable alloys contain tens of percents of a novel, "σ", Pu structure that we attribute to rearrangement of the Ga-depleted regions after the self-organization of the Ga to form quasi-intermetallic $Pu_{25-35}Ga$. This collective and cooperative behavior involving the Ga and other defects in terms of a tendency to aggregate into domains with structures that differ from the δ host and the resulting nanoscale heterogeneity also appears to play an important role in the observation of analogous locally ordered structures in aged materials. This description of these materials and their aging is radically different from current conceptual basis derived from other experiments that are insensitive to ordering on the angstrom–nanometer length scale.



INTRODUCTION

Because short wavelength X-ray and neutron diffraction are sensitive only to the long-range average arrangement of the atoms in the coherent portion of a crystal, complementary local structure measurements are required for a complete understanding of the structure of a complex material.[1−7] This is particularly an issue in solid solutions where even a random distribution of a solute will result in nanometer-scale fluctuations in the local composition. Such fluctuations are greatly enhanced if the solute (or charge or spin or defect) distribution is organized by collective and cooperative phenomena. These occur in the form of interactions between these inhomogeneities that control or at least influence their placement relative to each other to give static (with solutes or defects) or dynamic (with itinerant charge or spin) (quasi-) ordered structures. One consequence of this solute clustering would be that, when the local composition of sets of atoms deviates from the average enough to fall outside the phase boundaries of the bulk material, there would reside within the crystal domains that would be unstable in the structure of the host phase if they stood alone. If the tendency of these atoms to rearrange their structure as dictated by their phase diagram is greater than the pinning effect exerted by their host, then they may rearrange to form embedded domains at or below the

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