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Short-range atomic structure of 1 wt. % Ga δ-stabilized plutonium by x-ray-absorption fine-structure spectroscopy

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Using extended x-ray-absorption fine-structure (XAFS) spectroscopy we have determined the radii of the first three atomic shells around Ga and the first Pu shell in a fcc Pu alloy stabilized by 1 wt. % Ga. We find the Ga to be substitutional in the fcc lattice, with the first and second shells contracted by 3.7 and 0.9%, respectively, relative to distances expected from the lattice constant derived from x-ray diffraction. The lattice is well ordered around Ga, but there is considerable static disorder in all observed coordination shells of Pu. We discuss these results in relation to the mechanism by which Ga effects phase stabilization.

Both its alloying behavior and propensity for phase changes contribute to plutonium's reputation as being arguably the most enigmatic metal in existence. Between room temperature and the melting point Pu passes through six allotropic modifications with crystal structures ranging from monoclinic (α and β) phases to fcc (δ phase) and bcc (ε phase). Equally striking is the 16.9% density decrease between α and δ Pu. Although there can be little doubt that the $5f$ electrons play the principal role in these phenomena, clear-cut indications of $5f$ localization, such as the appearance of magnetism as occurs in Ce are lacking, as is a comprehensive theory incorporating the required correlated-electron effects.

The ability of Ga and a few other elements to maintain Pu in the fcc structure to ambient temperature is directly relevant to the questions surrounding its structural complexity and phase change behavior. Except for the preponderance of trivalency, it is difficult to identify any common properties in the list of δ-phase stabilizers. The (average) atomic volume ranges from 16.6 Å^3 (Al) to 33.8 Å^3 (Am). Except for Ga and Sc, the metals exist in the fcc structure either at ambient temperature or in a higher-temperature phase. Most of the metallic cohesion in Al and Ga comes from the p orbitals, whereas d bonding is dominant in Ce, Am, and Sc.

The stability conferred upon the Pu fcc structure by the addition of Ga is manifested in the thermal behavior of the alloys. Increasing the Ga concentration from 1 to 9 at. % raises the temperature at which the alloy transforms to the bcc ε phase by over 100 °C. A melting-point elevation is observed as well. In contrast to the negative coefficient of thermal expansion exhibited by unalloyed fcc Pu, the Ga-stabilized phase expands with increasing temperature, but shows a Ga-dependent coefficient. In addition, the elastic constants are anomalous (see below).[1]

Use of the term "δ stabilized" is somewhat misleading in describing these alloys, since at low Ga concentrations they are known to be metastable to pressure and/or low-temperature-induced reversion to higher-density phase(s). For these compositions "stability" is probably a kinetic rather than a thermodynamic phenomenon.

To better understand the mechanism by which Ga alloying stabilizes the δ phase of Pu, the local structure around the Ga and Pu atoms was examined by x-ray-absorption fine-structure (XAFS) spectroscopy. XAFS determines the local environment around a particular atomic species absorbing the x-ray energy. Thus the local structure around the Ga and Pu atoms can be investigated independently. This method provides information complementary to x-ray-diffraction (XRD) methods, which only measure the average crystallographic structure.

The samples were mounted in a copper cell with Kapton windows, fastened to the cold finger of a LN cryostat, and held at 80 K. Spectra were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL) on end-station 4-2 under dedicated operating conditions (3.0 GeV and 40–80 mA) using Si (220) monochromator crystals. The relative orientation of the crystals was tuned to provide maximum intensity; a flat Rh-coated mirror was used to reject harmonics. All measurements were made in the fluorescent mode using a 13-element Ge detector positioned perpedicular to the beam. The sample, a 30-μm-thick foil was positioned at 45° in relation to both the incident x-ray beam and the detector.

The spectra were reduced in the standard way.[2] The energy was calibrated by defining the inflection points of the first features in the Ga K and Pu L_{III} edges of the pure metals as 10 368.7 eV and 18 059.0 keV, respectively, and the corresponding ionization thresholds (E_0) were defined as 10 385 and 18 075 eV. Polynomials were fit through the pre-edge and post-edge regions. The data were normalized by setting the pre-edge polynomial to zero and the difference between these to unity at E_0. The XAFS was determined as the difference between the spectra and a polynomial spline fit to the post-edge region normalized by Victoreen function as defined in the report of McMaster *et al.*[3] The polynomial spline was adjusted to minimize the area of the low-frequency ($R < 1.1$ Å) region of the Fourier transform without reducing the amplitudes of features corresponding to structural components.

Due to the high concentration and thickness of the Pu, the amplitude of the XAFS was corrected for self-absorption effects by dividing by 0.388, the average value of the self-absorption coefficient over the energy range of the XAFS data, according to the procedure of Tröger *et al.*[4] and Stern and Heald.[5] Since the concentration of Ga in these samples is small (3.3 at. %), negligible self-absorption effects (on the order of 5%) are expected in the Ga-edge spectra.

k^3 weighting was used throughout the analysis since the Debye-Waller factors are apparently large, and the resultant damping effect maintains approximately constant amplitude of the XAFS up to high k with this weighting (Fig. 1).

Curve fits were performed utilizing phases and amplitudes calculated by the FEFF program.[6] Both single- and multiple-scattering paths from the FEFF calculation were used. The data were fit to the single-scattering formula:

$$\chi(k)=S_0^2\sum_j A_j(k)\sin[2kR_j+\Phi_j(k)] , \tag{1}$$

where

$$A_j(k)=(N_j/kR_j^2)f_j(k)e^{-2k^2\sigma^2}e^{-2R_j/\lambda} ,$$

where the amplitude factor S_0^2, Debye-Waller factor σ_j, and the average bond length R_j were used as fitting parameters. The energy defining $k=0$, E_0, entered indirectly as a fitting parameter through the relation:

$$k=\sqrt{2m(E-E_0)}/\hbar . \tag{2}$$

The coordination numbers of the various shells, N_j, were held fixed to the number known to exist in the first, second and third shells of a face-centered-cubic (fcc) lattice (i.e., were held to 12, 6, and 24, respectively). The amplitude was allowed to vary through the structure factor S_0^2, and the Debye-Waller contributions. The complex photoelectron scattering factor $f_j(k)$ was calculated using the code of FEFF (Ref. 6) for both single- and multiple-scattering paths.

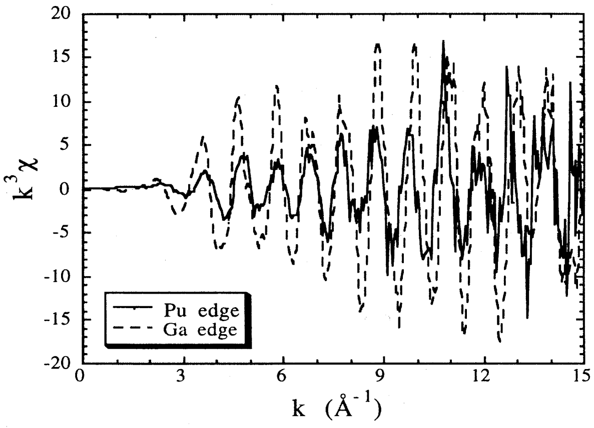

FIG. 1. Extended x-ray-absorption fine structure of Pu and Ga edges. The Pu data have been corrected for self-absorption effects.

Comparison of the two spectra shows that, despite (see below) the similarity of the local environment of the first coordination shell (in terms of the numbers and types of atoms), the amplitude of the Pu XAFS is much less than that of the Ga (Fig. 1). This result is also easily observed in the Fourier transform moduli (Fig. 2). The contributions of the individual shells around the Ga [Fig. 2(a)] are easily resolved in that they are symmetric, large amplitude, and approach zero between the peaks. In contrast, the peaks in the modulus for $R > 3.5$ Å, containing the contributions of the second and higher shells around the Pu [Fig. 2(b)], are much lower in amplitude, broader, and contain additional fine structure consisting of shoulders and satellite peaks. It is therefore much more difficult to identify and separate the contributions to the Pu XAFS of the individual shells.

The contribution of Ga neighbor atoms to the XAFS is negligible and, to within the resolution of the technique, the XAFS of both the Ga and the Pu reflect only Pu near neighbors. Curve-fitting results (see below) demonstrate that the Ga is not present as clusters. Such Ga clustering would create overlap of the attendant large strain fields, and is probably energetically unfavorable. To first order, the Fourier transform (FT) of the Ga and Pu XAFS should be similar, with perhaps some shifts in position due to the smaller metallic radius of Ga and the difference in phase shift. However, we observe large discrepancies between the two FT's. Since both the Ga and Pu are surrounded by Pu and the site symmetry is expected to be the same, the structure of the higher-order shells in the FT's should be similar. In these respects the spectrum and, by inference, the local structure about the

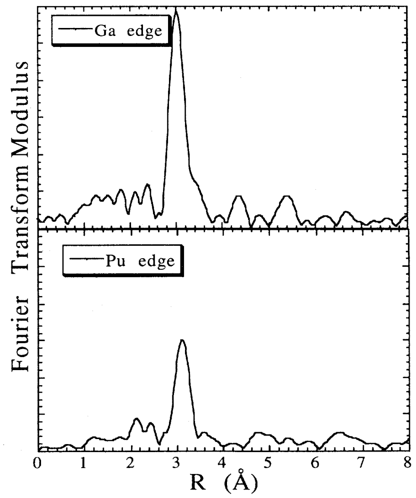

FIG. 2. Fourier transform moduli of the Ga and Pu XAFS spectra. The transform region for both spectra is $2.72 < k < 14.84$, and both are plotted on the same scale. A Gaussian window of 0.1 Å^{-1} was used for both data sets.

Ga ions is much more similar to typical fcc metals (e.g., Pt, Cu) than that which we find for the Pu atoms. The Pu XAFS FT contains much broader and more complex higher-order peaks than the Ga FT, which indicates that, although the average positon of the neighbor atoms corresponds to a fcc structure, there is corresponding complexity in the distributions of the atoms in the successive shells around the Pu atoms.

The crystallographic lattice parameter for pure δ Pu is 4.64 Å. Alloying with Ga decreases the average lattice parameter, and the value for 1 wt. % Ga (3.3 at. %) is approximately 4.61 Å.[7] Using the value of the average lattice parameter for the Pu-Ga alloy, the calculated distances are 3.26 Å for the first shell ($\langle \pm\frac{1}{2}a, \pm\frac{1}{2}a, 0 \rangle$); 4.61 Å for the second shell, ($\langle \pm a, 0, \rangle$); and 5.65 Å for the third shell ($\langle \pm\frac{1}{2}a, \pm\frac{1}{2}a, \pm a \rangle$). The corresponding distances in pure Pu are 3.28, 4.64, and 5.68 Å, respectively.

Metrical information from the XAFS for comparison was obtained by curve fits. The Ga XAFS data were fit over the range $2 < k < 14.4$ Å. Correspondence between the fit and the data was very good throughout this region (Fig. 3), especially for the phase. The somewhat poor quality of the fit at the extremities of this range is attributed to distortions due to Fourier transforming. For Ga, the Ga-Pu first shell distance refines to a distance of 3.14 Å, the second shell to 4.57 Å, and the third shell to 5.62 Å. Because the numbers of atoms in a fcc structure are known, the coordination number was held constant and the scale factors were allowed to vary. Under these conditions, the scale factors and Debye-Waller factors increased together. The scale factors were then held fixed at the value obtained for the first shell, 0.9, and the Debye-Waller factors were allowed to vary. The quality of the fit was < 10% worse than the best fit obtained by varying all parameters. The Debye-Waller factors (σ) for all three shells are very reasonable, in the range $0.068 < \sigma < 0.095$, with σ increasing with increasing distance from the central atom, as expected. The correspondence of the fit with the data indicates that modeling the disorder using a sample Gaussian distribution works well, inferring that the structure of the Pu around the Ga is well ordered.

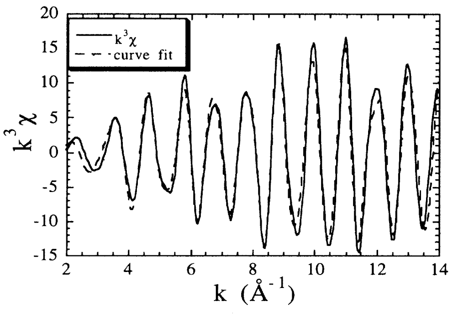

FIG. 3. Ga edge XAFS data and curve fit to three Pu occupied shells. The data were first backtransformed about each of the contributions of the individual shells, the data for each shell were curve fit separately and the results of these preliminary fits were used as the initial parameters to subsequently perform this multiple shell fit over the entire pertinent data range.

The distances determined for the first, second, and third shells around the Ga atom are smaller than the average lattice parameters for 3.3 at. % Ga in the Pu alloy system. The discrepancy between the measured and expected distances for the successive shells decreases with increasing distance from the central atom. The first shell is 0.12 Å smaller; the second shell, 0.05 Å smaller; and the third shell is 0.04 Å smaller than expected from the crystallographic lattice parameters. The presence of Ga in the Pu structure orders the Pu and induces a strain field that contracts the bond lengths in proximity to the Ga, but the structure relaxes back to the Pu structure within a few coordination shells.

In the Pu edge data, the only shell whose position we were able to determine accurately is that of the first shell, located 3.29 Å from the absorbing atom. However, as discussed below, the local lattice distortion around Ga also creates bond length variations (static disorder) around Pu which depends on its proximity to the impurity atom. The proper interpretation of the near-neighbor distance from the fitting procedure is not entirely clear, since it represents an average of at least three or four different Pu environments. Therefore we do not believe too much significance should be attached to the fact that the near-neighbor distance is slightly larger than XRD would predict in an ideal fcc structure.

Part of the Pu disorder can be described in detail by considering the bond length variation associated with the 12 Pu atoms in the first shell around a Ga atom. Note that in the 3.3 at. % Ga alloy these Pu atoms represent 39.6% of the total. By reconstructing the structure around the Ga atoms, we find that each Pu atom has 5 (4 Pu and 1 Ga) nearest neighbors within the $GaPu_{12}$ cluster at a distance of 3.14 Å. Its two neighbors in the second sphere are 3.23 Å away, and the four in the third sphere are 3.30 Å distant. One near neighbor ($\langle \pm a, \pm a, 0 \rangle$) is in the fourth sphere at 3.38 Å. Thus a difference of 0.24 Å exists between the shortest and longest bond(s). Also, the metallic radius of the first shell atoms, based on the average bond length, is 1.61 Å, which is 1.8% smaller than the nominal δ radius. Since the average atomic radius of Pu in the material must agree with the measured lattice constant, one can easily show that the average radius of Pu atoms not coordinated to Ga (1.64 Å) is that found by extrapolating the alloy lattice constant to zero Ga concentration. The latter sites will also exhibit varying degrees of anisotropy. XAFS measurements on Pu alloys with different Ga concentrations are in progress, and should provide additional insight into the sources of static disorder around Pu.

Both phenomenological approaches and electronic-structure calculations have been employed to understand the response of a metal lattice to an impurity atom. The former treat the metal as an isotropic elastic medium and employ elastic constants such as compressibility, bulk or sheer moduli, or Poisson's ratio to describe atomic displacements near an impurity and lattice constant changes. This formalism has been surprisingly successful given the uncertain applicability of macroscopic properties to atomic-scale displacements. Band-structure calculations are considerably more laborious, but provide a much more detailed look at the bonding interactions underlying the local structure. However, band-structure calculations are limited by their assumptions (i.e., one-electron model) in elucidating the correlated-electron effects expected in Pu alloys. Also, their failure to give accurate near-neighbor distances in some cases signals the presence of electronic properties, e.g., magnetism, which are beyond the scope of the theory.

The XAFS study of Scheuer and Lengeler[8] of a large number of impurity elements in eight solvent metals permits a comparison of the Pu-Ga system with more familiar alloys and with the prediction of elastic theory. For the change in nearest-neighbor distance, Δr_1, these authors derive Eq. (2) from the work of Eshelby:[9]

$$\Delta r_1 = f_\Omega \frac{\sqrt{2}}{8\pi\gamma} r_1 \ . \qquad (3)$$

Here f_Ω is the normalized rate of change of atomic volume with respect to solute concentration, γ is the Eshelby constant, $\gamma = 3(1-\nu)/(1+\nu)$, and ν is Poisson's ratio (0.26 for fcc Pu). From the lattice constant data of Ellinger, Land, and Struebing,[7] one obtains $f_\Omega = 0.551$, which yields $\Delta r_1 = .058$ Å. This compares with the experimental value of 0.12 Å. Both the experimental magnitude of the first-neighbor shift and the discrepancy between this value and the prediction of elastic theory are larger than for any metal-impurity pair reported in Ref. 8. One reason for the poor agreement is the large elastic anisotropy of this alloy,[1] which exceeds that of any other fcc metal. Poor agreement with elastic theory is not unique to the Pu-Ga system; attempts to rationalize deviations from Vegard's law are uniformly less accurate for alloys in which the solute is smaller than the solvent atom.

The simple (by x-ray diffraction) crystal structure and linear dependence of the lattice constant on impurity concentration seem to indicate that Ga-stabilized fcc Pu alloys are simple random substitutional solid solutions. Our XAFS results as well as several other properties of these materials show quite clearly that such a description is inaccurate. At a Ga concentration of 3.3 at. % nearly 40% of the lattice atoms are coordinated to Ga. If site occupation were random, approximately this fraction of the Ga atoms would have at least one Ga nearest neighbor. Such clustering would measurably perturb the spherical symmetry expected in a fcc lattice and found by XAFS. In addition, Ga induces a large strain field in the Pu, and strain fields tend to repel each other, thus it appears that greater stability would be achieved by maintaining the maximum number of Pu atoms around each Ga atom. Although no evidence of Ga ordering has been reported, its apparent tendency to maintain the greatest possible separation suggests a superlattice structure may be present. Up to 6.25 at. % Ga can be accommodated in a bcc arrangement with a lattice constant twice that of the parent fcc lattice. Higher concentrations require populating ⟨100⟩-type sites with Ga atoms being shared by adjacent $GaPu_{12}$ clusters. The high-temperature form of Pu_3Ga exists in the Cu_3Au structure which maintains the 12-Pu-atom coordination sphere. It is interesting that the Pu-Ga distance has increased by only 0.04 to 3.18Å for a 21.7 at. % increase in Ga concentration. This seems to imply that the largest modification of the electronic structure of Pu occurs with the substitution of one nearest-neighbor by Ga; additional Ga near neighbors effect considerably smaller changes.

In addition to determining local atomic structure the x-ray-absorption process probes the empty density of states (DOS) of appropriate l value near the atom of interest. For Ga one observes, as dictated by dipole selection rules, $1s \rightarrow 4p$ transitions which directly reflect changes in the DOS from the Ga orbitals most involved in bonding. Comparison of the Ga x-ray-absorption near-edge spectra (XANES) in the Pu-Ga alloy with that of Ga metal indicates that the electronic structure of the Ga has been significantly altered by alloying with Pu. Figure 4 shows the Ga edges for the 3.3 at.% Ga-Pu alloy and Ga metal. The most striking aspect of the spectra is the transfer of spectral weight from just above the Fermi energy (region A) in Ga metal to the prominent peak at higher energy (region C) in the alloy. A band-structure calculation for α-Ga has been reported by Gong *et al.*[10] The pronounced bond-length variation present in the orthorhombic structure superimposes considerable structure on the parabolic DOS expected for a free-electron-like material. In particular, the Ga atoms separated by only 2.44 Å (the average bond length is 3.03 Å) produce a pseudogap in the DOS at E_f. The weak shoulder (region A) in the XANES probably reflects this feature. The calculation also shows a high DOS from about 8–10 eV above E_f, in qualitative agreement with the XANES spectrum.

Guidance for interpreting the alloy spectrum comes from the band structure of Pu_3Ga.[11] While the Ga con-

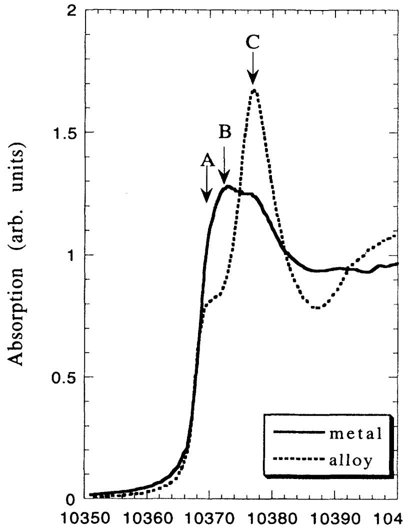

FIG. 4. Comparison of Ga absorption edges in Ga metal and 3.3 at. % Ga in Pu alloy.

centration in this material is higher than in the alloy of interest, it exists in the Cu_3Au structure and so is similar in that each Ga atom has 12 Pu nearest neighbors. The details of this calculation will be published elsewhere, but can be summarized as follows. Most of the Ga p states are found from about 1 to 3.5 eV below E_f, and exhibit features in the DOS which are very similar to those of the Pu d and s. This clearly shows that most of the Ga-Pu bond cohesion results from this hybridization. Some sharp structure closer to E_f indicating Ga p-Pu f bonding is also evident, but represents a much smaller contribution to the bonding than comes from the Pu d and s orbitals. The possible importance of the p-f interaction in terms of Pu f bonding/localization is unclear.

The calculation also shows a very low p DOS just above E_f, in agreement with the reduced spectral weight in this region in the XANES spectrum. In essence, the strong Pu-Ga interaction has opened a hybridization gap in the Ga DOS much more prominent than in Ga metal by pushing both occupied and unoccupied states away from E_f.

Weinberger, Boring, and Smith,[12] on the basis of their Korringa-Kohn-Rostoker calculations argued that the impurity (Ga, Al, or Sc) shifted the f band to higher energy and therefore reduced the number of f electrons participating in bonding. The XAFS results, on the other hand, show that strong Ga-Pu hybridization exits, as evidenced by the large lattice contraction, and thus suggest that the bond strength and directionality within these $GaPu_{12}$ clusters is the main source of (fcc) lattice stability.

In conclusion, we have measured the local environment around both the Pu and Ga atoms by XAFS. We find the structure of the Pu atoms around the Ga is very ordered with first-, second-, and third-neighbor distances of 3.14, 4.57, and 5.62 Å, respectively. The structure around the Pu atoms is extremely disordered, but has an average nearest-neighbor distance of 3.29Å, close to the value expected in pure δ phase Pu metal. The presence of the Ga atoms introduces local strain fields which relax with increasing distance from the Ga atoms. Finally, the electronic structure of the Ga atoms is altered by alloying in the fcc Pu structure, and is reasonably well described by a rigid-band picture.

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