PHYSICAL REVIEW B, VOLUME 63, 174111

Local atomic structure of α-Pu

F. J. Espinosa, P. Villella, J. C. Lashley, and S. D. Conradson
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

L. E. Cox, R. Martinez, B. Martinez, L. Morales, J. Terry, and R. A. Pereyra
Nuclear Materials Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 20 November 2000; published 16 April 2001)

The local atomic structure of α-Pu was investigated using x-ray absorption fine structure (XAFS) spectroscopy. XAFS spectra were obtained for a zone-refined α-Pu and the results were compared to 32-year-old and Ce-doped (0.34 at. %) samples. X-ray diffraction (XRD) patterns were also measured for the zone-refined and 32-year-old materials. The extent of the Bragg peaks showed that amorphization of the 32-year-old sample had not occurred despite the prolonged exposure to self-radiation. Analogous to metastable δ-Pu alloys, the local atomic structure around Pu for the zone-refined material shows the possible presence of noncrystallographic Pu-Pu distances. Conversely, the Ce and the 32-year-old sample show no evidence for such noncrystallographic distances. Disorder in the Pu local environment was found to be impurity dependent. The Ce-doped sample presented a larger Pu-Pu nearest neighbor disorder than the aged sample, although the total amount of Am, U, and He impurities was actually higher in the aged sample. The local environment around U and Ce impurities is consistent with these elements being in substitutional lattice sites. In addition, U and Ce do not introduce significant lattice distortion to their nearest neighbors. This is consistent with disorder being more related to the perturbation of the coupling between the electronic and crystal structure, or the Peierls–Jahn-Teller distortion that generates the monoclinic α-Pu structure, and less to strain fields produced in the vicinity of the impurities.

DOI: 10.1103/PhysRevB.63.174111 PACS number(s): 61.10.Ht, 61.82.Bg, 61.80.−x

I. INTRODUCTION

Among other properties, the structural diversity of Pu is unique among the elements. At ambient pressure Pu transforms into a succession of six crystallographic phases between room temperature and its melting point at 914 K. In addition, these transformations are accompanied by large, nonmonotonic volume changes, with a 25% difference between the cubic (fcc) δ phase and the monoclinic α phase.[1] The low-temperature α phase is highly unusual because it is a metal with an open low-symmetry (monoclinic) crystal structure. It is also the densest form of Pu. Mechanically it is a hard, brittle metal that is nevertheless soft vibrationally, with a Debye temperature of ~200 K.[2] The origin of these structural (and other) properties of Pu has generally been attributed to the fact that it marks the boundary between the itinerant and the localized $5f$ electron systems. From Th through Np, the atomic volume displays the parabolic decrease typical of transition metals as the number of bonding electrons increases. However, the volume of the actinides jumps up sharply from Np to Am, ascribed to the localization of the $5f$ electrons.[3] Pu is in the middle of this discontinuity, with α Pu slightly and δ Pu significantly above the trend through Np.

The explanation for the atomic volumes and the low symmetry structure of α-Pu has been a long-standing challenge for electronic structure methods. It is currently a testing ground for these methods due to the high directionality and the large density of states involved in f electron bonding.[4] Among explanations for the structure of α-Pu, recently, *ab initio* relativistic total energy calculations have explained the crystal structure of α-Pu in terms of a Peierls–Jahn-Teller–like distortion.[5] This distortion splits a large $5f$ density of states (DOS) that crosses the Fermi energy in a higher symmetry cell. Thus, the total energy is minimized by lowering the symmetry of the crystal, resulting in the monoclinic α phase.[6]

Conventional crystallographic methods solve α-Pu as a monoclinic structure with 16 atoms per unit cell, space group $P21/m$, with eight unique atoms. All the atoms are located at either $(x,1/4,z)$ or $(-x,3/4,-z)$ positions. Six of the eight unique Pu atoms form four short bonds in the range 2.57–2.78 Å and ten long bonds in the range 3.19–3.71 Å. The seventh Pu atom forms five short and seven long bonds and the eighth unique atom forms three short and thirteen long bonds.[7] Although the directionality of the $5f$ orbitals suggests bonds with covalent character and electronic localization as the origin of the local asymmetry, calculations instead find the Peierls–Jahn-Teller–like distortion. The identification of nanometer-scale heterogeneity or phase separation in metastable δ-Pu alloys together with the structural complexity of the α phase suggests that α-Pu is a good candidate for local deviations from the average structure.[8] It is therefore of interest to determine if similar collective lattice distortions occur in the α phase, implying that they are intrinsic to Pu, or whether they only occur in and are specific to δ alloys. It is also of interest to determine if dopants have effects on the local structure of α-Pu analogous to those in the δ alloys.

The effects of trace elements, i.e., those occurring at concentrations well under one atom per unit cell, also raise the more general issues of the coupling of the induced local strain fields and disruption of the band structure around these defect sites to the solubility of the dopant element and its effects on the phase stability and other properties of the host.

0163-1829/2001/63(17)/174111(8)/$20.00