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A fully-relativistic full-potential-linearized-augmented-plane-wave study of the (1 1 1) surface of δ-Pu

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Abstract

Full-potential linearized-augmented-plane-wave calculations indicate that the antiferromagnetic state including spin–orbit coupling effect is the ground state of bulk δ-Pu with a lattice constant of 8.66 a.u. and a bulk modulus of 32.8 GPa. It is found that spin-polarization and spin–orbit coupling effects play competing roles in the localization to delocalization behavior of 5f electrons. The optimized lattice constants of δ-Pu bulk are used to calculate the electronic structure properties of δ-Pu(1 1 1) films up to seven layers at six theoretical levels, namely non-spin-polarized-no-spin–orbit-coupling (NSP-NSO), non-spin-polarized-spin–orbit-coupling (NSP-SO), spin-polarized-no-spin–orbit-coupling (SP-NSO), spin-polarized-spin–orbit-coupling (SP-SO), antiferromagnetic-no-spin–orbit-coupling (AFM-NSO), and antiferromagnetic-spin–orbit-coupling (AFM-SO). For the δ-Pu (1 1 1) films also, AFM-SO is found to be the ground state. For the films, surface energy rapidly converges and the semi-infinite surface energy is predicted to be 1.16 J/m^2. On the other hand, the magnetic moments show an oscillating behavior, gradually approaching the bulk value of zero with increase in the number of layers. It is also predicted that the work function of δ-Pu(1 1 1) films at the AFM-SO ground state is approximately 3.41 eV, and the work function shows some oscillations when the number of layers is less than five, while it becomes relatively stable when the number of layers is greater than five. This suggests that a 3-layer film might be sufficient for computations of, for example, adsorption energies while a 5-layer film may be necessary for precise computations of, for example, adsorbate-induced work function shifts. The calculated results are compared with other experimental and theoretical results in the literature and the agreements between them are excellent, given the complexity of the physical systems and different computational formalisms.

Keywords: Density functional theory; Generalized gradient approximation; Delta-plutonium; (1 1 1) Surface; FP-LAPW method

1. Introduction

Plutonium (Pu) is arguably the most complex metallic element known to mankind and has attracted extraordinary scientific and technological interests because of its unique properties [1–9]. First, Pu has, at least, six stable allotropes between room temperature and melting at atmospheric pressure, indicating that the valence electrons can hybridize into a number of complex bonding arrangements. Second, plutonium represents the boundary between the light actinides, Th to Pu, characterized by itinerant 5f electron behavior, and the heavy actinides, Am and beyond, characterized by localized 5f electron behavior. In fact, the high temperature fcc δ-phase of plutonium exhibits properties that are intermediate between the properties expected for the light and heavy actinides. Third, plutonium undergoes a 25% increase in volume when transformed from its α-phase (which is stable below 400 K) to δ-phase (stable at around 600 K), an effect which is crucial for issues of long-term storage and disposal.

Though the published literature on bulk Pu continues to grow [10], surface studies of Pu remain few and far between. In reality, surface study of Pu is also very important,

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from both scientific and technological points of views. It is believed that the unusual aspects of the bonding in bulk Pu are apt to be enhanced at a surface or in a thin layer of Pu adsorbed on a substrate, as a result of the reduced atomic coordination of a surface atom and the narrow bandwidth of surface states. For this reason, Pu surfaces and films may provide a valuable source of information about bonding in Pu, since the initial crossover from delocalized to localized behavior probably takes place at the Pu surface. Moreover, the surface corrosion of Pu in the presence of environmental gases is a problem not only scientifically and technologically challenging but also environmentally important. For theoretical studies of surfaces, it is common practice to model the surface of a semi-infinite solid by an ultra-thin film (UTF), thin enough to be treated with high-precision density functional calculations, but thick enough to model the intended surface realistically. Determination of an appropriate UTF thickness is complicated by the existence of possible quantum oscillations in UTF properties as a function of thickness; the so-called quantum size effect (QSE). These oscillations were first predicted by calculations on jellium films [11,12] and were subsequently confirmed by band structure calculations on free-standing UTFs composed of discrete atoms [13–16]. The adequacy of the UTF approximation obviously depends on the size of any QSE in the relevant properties of the model film. Thus, it is important to determine the magnitude of the QSE in a given UTF prior to using that UTF as a model for the surface. This is particularly important for Pu films, since the strength of the QSE is expected to increase with the number of valence electrons.

In the present study, UTFs of fcc Pu δ-phase, instead of α-phase, are selected for investigation, based on the following considerations. First, δ-Pu is technologically more important than α-Pu. Known to be monoclinic with sixteen atoms per unit cell, the ambient ground-state α-phase is very brittle and not suitable for engineering applications, whereas Pu δ-phase is more ductile and useful in practice. Also, although the monoclinic α-phase of plutonium is more stable under ambient conditions, there are advantages to studying δ-like layers. First, a very small amount of impurities can stabilize δ-Pu at room temperature. For example, $Pu_{1-x}Ga_x$ has the fcc structure and physical properties of δ-Pu for $0.020 \leqslant x \leqslant 0.085$ [17]. Second, grazing-incidence photoemission studies combined with the calculations of Eriksson et al. [18] suggest the existence of a small-moment δ-like surface on α-Pu. Our work on plutonium monolayer has also indicated the possibility of such a surface [19]. Photoemission results by Arko et al. indicate that both α- and δ-phases of Pu display a narrow, temperature-independent, 5f-related feature at the Fermi energy, narrower in δ-Pu than in α-Pu, suggestive of possible heavy-fermion-like behavior [20]. Recently, high-purity ultra-thin layers of plutonium deposited on Mg were studied by X-ray photoelectron (XPS) and high-resolution valence band (UPS) spectroscopy by Gouder et al. [21]. They found that the degree of delocalization of the 5f states depends in a very dramatic way on the layer thickness and the itinerant character of the 5f states is gradually lost with reduced thickness, suggesting that the thinner films are δ-like. At intermediate thickness, three narrow peaks appear close to the Fermi level and a comparative study of bulk α-Pu indicated a surface reorganization yielding more localized f-electrons at thermodynamic equilibrium. Also, δ-plutonium shows negative thermal expansion coefficient and exhibits superconductivity alloyed with other elements. Finally, it may be possible to study 5f localization in plutonium through adsorptions on carefully selected substrates for which the adsorbed layers are more likely to be δ-like than α-like.

Regarding δ-Pu surface, there are *very few* theoretical calculations in the literature. Using the self-consistent film-linearized muffin-tin-orbital (FLMTO) method, Hao et al. studied the electronic structures of the (1 0 0) and (1 1 1) surfaces using five-layer slab geometries [18]. The calculated work functions for the systems were found to be 3.68 eV and 4.14 eV, respectively, with the 6p electrons treated as core states. They obtained a much higher value of 8.4 eV, if the 6p electrons were treated as valence electrons. Ray and Boettger used linear combinations of Gaussian-type orbitals-fitting function (LCGTO-FF) method to study δ-Pu(0 0 1) and (1 1 1) films up to five layers. Because of highly compute-intensive nature of this method, spin-polarization was not included in these calculations beyond the di-layer. They found that the surface energies converged within the first three layers, while the work function exhibited a strong QSE [22]. Using the full-potential linearized-augmented-plane-wave (FP-LAPW) method, Wu and Ray [23] have investigated bulk δ-Pu and the (0 0 1) surface up to seven layers at the non-spin-polarized-no-spin–orbit-coupling (NSP-NSO), non-spin-polarized–spin–orbit-coupling (NSP-SO), spin-polarized-no-spin–orbit-coupling (SP-NSO), spin-polarized-spin-polarized-coupling (SP-SO) levels of theory. The surface energy was again found to be rapidly converged at all four levels of theory and the semi-infinite surface energy was predicted to be 0.692 eV at the SP-SO level of theory. The present study is an extension of this work for the Pu (1 1 1) surface up to seven layers but here we have considered six levels of theory, namely the four mentioned above but also antiferromagnetic-no-spin–orbit-coupling (AFM-NSO), and antiferromagnetic-spin–orbit-coupling (AFM-SO). Since the lattice constants used in the surface calculations are the same as optimized bulk lattice constants, we first have extended our previous calculations for bulk δ-Pu at the AFM-NSO and AFM-SO levels. Because of *severe* demands on computational resources due to the large system sizes involved, no *further* surface relaxations and/or reconstructions have been taken into account. We did relax the 1-layer film to get an idea of the effects of this approximation as discussed below. It is believed that the qualitative and the quantitative trends in the results reported below should hold true in any future detailed investigations taking into account surface reconstructions and/or relaxations.