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Vacancy formation in δ-plutonium: A density-functional study in the generalized gradient approximation

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Abstract. – The defect population is important for understanding the microstructure of δ-plutonium. Using spin-polarized density-functional theory, we calculate the formation energies of monovacancies as well as divacancies. We show that the unrelaxed values are quite independent of the magnetic configuration while atomic relaxations lead to smaller values, relaxation effects being larger for the disordered magnetic structure.

Introduction. – Fcc or δ stabilized phase of plutonium is an important technological material and one of the most tricky problems concerning this alloy involves predicting its properties under long-term aging. Due to its radioactive nature, the unstable plutonium nucleus decays principally by α-decay. The decay event produces two energetic nuclear particles: an α particle and a recoil uranium nucleus. This last heavy element converts three-quarters of its energy into atomic displacements and causes most of the initial damage in the plutonium lattice. Each α particle captures two electrons from the plutonium metal and comes to rest in the lattice as helium atoms. The interactions of the surviving defects with the microstructure and their evolution as a function of time and temperature determine the extent of self-irradiation effects on the properties of plutonium. Two types of defects, namely vacancies and self-interstitials, are formed in metals under irradiation. The evolution of defect population leads to significant changes in the microstructure and causes a number of radiation-induced macroscopic properties changes such as density, ductility or elastic constants.

Due to the special location of plutonium at the boundary between light actinides (delocalized $5f$ electrons) and heavy actinides (localized $5f$ electrons) a slight change in atomic volume or internal stresses could affect its stability.

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Such a complexity still increases when plutonium is alloyed with Al or Ga. As the respective phase diagrams indicate an eutectoid decomposition of the δ phase to the alpha phase plus the Pu_3M compound at low composition and temperature [1], a demixtion could occur during aging. Hence, such a non-equilibrium structure should be subject to change during long-term aging and could compromise structural δ phase integrity.

Concerning the knowledge of the thermodynamic and kinetic behavior of metals, one of the most important quantities is the vacancy formation energy. It determines the equilibrium vacancy concentration and contributes to the self-diffusion coefficient in the monovacancy mechanism, which is the main diffusion process in the closed-packed metals. Then the activation energy is the sum of the vacancy formation energy and of the migration energy of the vacancy. Due to the lack of experimental values concerning defects in plutonium and its alloys, first-principles calculations are of considerable interest to estimate the formation energies of point defects in these phases. To this aim, we study the stability and formation energies of vacancies in plutonium using PAW-based calculations (VASP Package [2, 3] method).

Even if magnetism in δ-Pu has not been confirmed by experiment [4], taking into account magnetic exchange interaction leads to major improvements compared to standard non-magnetic LDA or GGA results [5–7]. As already shown in our previous papers [8, 9], spin-polarized GGA approximation is able to reproduce the main equilibrium properties and energy differences of pure and alloyed plutonium. Many phase stability properties of the Pu-X (X = Al, Ga, In) alloys [10] can be represented by coupling these results with a statistical approach (Cluster Variational Method) [11, 12].

In the present paper, we follow these ideas and expand the investigation to study the influence of magnetic configuration on the vacancies energies in δ-plutonium. The calculations were performed for three different configurations, namely: antiferromagnetic (AF), ferromagnetic (FM) and disordered magnetic structures (DM). We also evaluate box-size effects and local relaxations with these three magnetic configurations.

The paper is organized as follows. Details of the electronic structure calculations are discussed in the second section. Results and a discussion are presented in the third and fourth sections.

Computational details. – We have performed spin-polarized PAW calculations using the Vienna *ab initio* simulation package VASP [2,3]. The PAW method [13] in the implementation of Kresse and Joubert [14] is used to describe the electron-ion interaction. The calculations include 16 valence electrons for Pu with the semicore $6s$ and $6p$ states and a plane-wave cutoff of 264.2 eV. Generalized gradient corrections are added in the form of the Perdew-Wang [15] functional and the spin interpolation of Vosko *et al.* [16] is used.

For a supercell containing N sites, the energy $E(N)^f_{N_v}$ required to form N_v vacancies is the difference between the energy of a system of N atoms with N_v vacancies $E(N - N_v, N_v)$ and the energy of a perfect crystal of N atoms $E(N, 0)$,

$$E(N)^f_{N_v} = E(N - N_v, N_v) - \frac{N - N_v}{N} \cdot E(N, 0). \tag{1}$$

In the limit of large N, this energy will converge to the formation energy for isolated vacancies and equilibrium volume will not be modified. As we must use finite-size supercells (periodic conditions and computational limits), we test three different supercell sizes with 54, 108 and 256 atoms.

We have used a bct unit cell with $c/a = \sqrt{2}$ to build the 54-atom supercell while fcc unit cells have been used for 108- and 256-atoms supercells. In our approach, the first vacancy

TABLE I – *Formation energies of monovacancy for FM, AF and DM configurations in* eV.

	54	108	108	256
	$8\,k$ points	$4\,k$ points	Γ-point	Γ-point
FM-unrel.	1.64	1.53	1.51	1.54
AF-unrel.	1.71	1.61	1.56	1.60
DM-unrel.	1.40	1.62	1.57	1.59
FM-rel.	1.56		1.28	1.31
AF-rel.	1.48		1.34	1.36
DM-rel.	0.97		1.07	1.08

is placed on a corner of the supercell and the second vacancy is located as first neighbor of this corner.

To describe the disordered magnetic configuration, we use a random mixture of spin-up and spin-down obtained by a Monte Carlo algorithm, the total magnetic moment of the supercell being equal to zero. Four different configurations have been used to produce average values. For the three different magnetic configurations, the equilibrium volumes of non-defective structures have been determined by fitting five total energies of 54-atom supercells as a function of Murnaghan's equation of state. The calculated values, *i.e.* (27.0, 24.0 and 23.5 Å/atom for FM, DM and AF) are in good agreement with previous published results [6, 8]. Let us mention that the spin-orbit coupling has not been included in the present calculations. We have checked this effect in the case of FM configuration. We obtained that the spin-orbit coupling leads to a smaller volume of 3%. Therefore, although important for the finer details of the results, spin-orbit is not essential for the present quantitative study of vacancy formation energies in δ-plutonium [6].

Total energy calculations are performed with a Gaussian smearing approach ($s = 0.2\,\text{eV}$) in the framework of Methfessel-Paxton method. The reciprocal space sampling was performed with $8\,k$ points for 54-atom supercells while the gamma point was used for both 108-atom and 256-atom supercells. $4\,k$ points have been also used for 108-atom supercells to check the convergence of our results. The ionic positions are optimized using a conjugate-gradient algorithm until the vector components of the force on any atom were less than 0.01 eV per Å.

Results and discussion. – Unrelaxed and relaxed values of vacancy formation energies are reported in tables I and II. Let us first discuss the effect of the supercell size. In our calculations, we used 54-, 108- and 256-atom supercells in investigating this issue. For all magnetic configurations, the energy differences between 108- and 256-atom supercells is of order of 3%, which may be considered as well converged. We have also studied the k-point

TABLE II – *Formation energies of divacancy for FM, AF and DM configurations in* eV. *The formation energies are divided by two.*

	54	108	256
	$8\,k$ points	Γ-point	Γ-point
FM-unrel.	1.59	1.48	1.50
AF-unrel.	1.59	1.54	1.57
DM-unrel.	1.42	1.56	1.56
FM-rel.	1.48	1.24	1.25
AF-rel.	1.43	1.31	1.34
DM-rel.	0.78	1.01	1.01

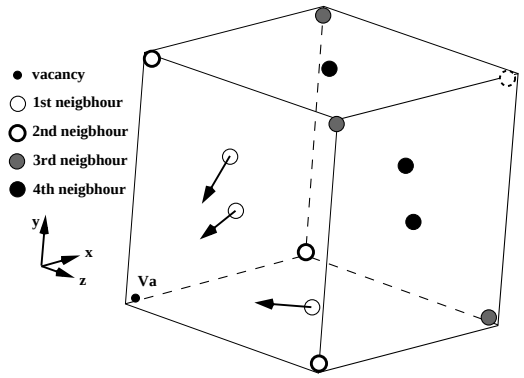

Fig. 1 – The force field of unrelaxed Pu atoms around the vacancy (108-atom supercell) calculated whithin AF or FM configurations. Longer arrows indicate longer forces (see text). Neighbors are related to *Va*.

convergence for the unrelaxed values, using 108-atom supercells. We can note that the k-point convergence is already obtained for the gamma point only.

The first interesting result is that the unrelaxed values of both mono and divacancies are not very sensitive to the long-range magnetic ordering. This is due to the fact that the bonding properties of δ-Pu originate mainly in the formation of a local spin moment in Pu atoms which strongly modifies the hybridization of the $5f$ states with other s, p, and d states with respect to non-magnetic calculations [17]. A similar result has been also obtained in Pu-Ga and Pu-Al alloys [9]. We have also to note that the vacancy formation energy represents around 40% of the Pu cohesive energy (3.8 eV in our calculations) as usual for transition metals [18].

The other important point is that the formation of divacancies does not require an additional energy with respect to the formation of two isolated monovacancies. Therefore, it may be thought that vacancy clusters are as stable as isolated vacancies. Such vacancy clusters eventually lead to the nucleation and subsequent growth of voids. However, it is clear that such a process is thermally activated via the diffusion of monovacancies to form clusters.

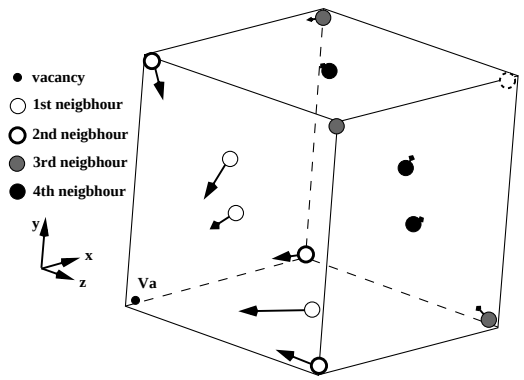

Fig. 2 – The force field of unrelaxed Pu atoms around the vacancy (108-atom supercell) calculated whithin DM configuration. Longer arrows indicate longer forces (see text). Neighbors are related to *Va*.

Let us now discuss the relaxed values of both mono- and divacancies. For each magnetic configuration, the energy of the divacancy is still similar to the energy of two isolated vacancies. The main result is that the relaxed energy is more important for the disordered magnetic configuration than for the two ordered ones. In figs. 1, 2, we have reported the force field on unrelaxed Pu atoms around the vacancy *Va* for the disordered magnetic configuration, DM, as well as for the ordered ones, AF or FM. Similar results are obtained for both ordered magnetic configurations: the first-nearest-neighbor shell dominates the relaxation energies ($\simeq 0.2\,\mathrm{eV/\AA}$ for monovacancy). When the second vacancy *Vb* is created to form the divacancy, the behavior is the same and the resulting forces acting on atoms point to the barycenter of the divacancy ($\simeq 0.3\,\mathrm{eV/\AA}$). We also notice that the inward relaxation is of order of 3% (7% for divacancies), as usually obtained for transition metals. We obtained the same trend for AF than for FM although AF Pu is known to be unstable with respect to a small tetragonal distorsion which is also volume dependent [7, 8]. This is due to the fact that relaxation effects concern only first-nearest neighbors and do not imply any phonon-based mechanism. For DM, the geometry of the force field on Pu atoms around the vacancy is more complex. If forces on the unrelaxed first-shell atoms are still important ($\simeq 0.2\,\mathrm{eV/\AA}$), forces on unrelaxed second-shell atoms are now non-negligible ($\simeq 0.1\,\mathrm{eV/\AA}$). Such a behavior must be related to the absence of the long-range magnetic ordering. In this case, more complex variations of the local spin moment in Pu are allowed according to their location with respect to the vacancy.

Let us mention that our calculated values are larger than the theoretical one, 0.5–0.66 eV, obtained using molecular-dynamical simulations in the framework of MEAM potential. In the absence of any experimental data [19], we can suggest that our first-principles–based values can be utilized for developing more efficient interatomic potentials for plutonium [20, 21].

Conclusion. – We have studied vacancy formation energies of δ-plutonium when magnetic exchange interaction is taken into account. Although any kind of magnetic order has never been observed in plutonium, the presence of a local magnetic moment could not be excluded as well as Kondo-like effects [22]. Here we demonstrate that this interaction is essential to predict a correct equilibrium volume and therefore the vacancy formation energies in this phase.

We find that random ordering of the spins leads to the lowest values of the formation energy of both mono- and divacancies, mainly due to a peculiar relaxation of Pu atoms around these defects. We have also shown that divacancies are as stable as monovacancies. Such a result may provide an explanation of the formation of vacancy clusters under radiation.

More generally, in the framework of plutonium research, we hope that our results can be used in a future description of thermodynamic properties of this enigmatic actinide. This knowledge is crucial in order to assess long-term aging behavior of plutonium and its alloys.

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