

UCRL-TR-215883



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Calculational Study on the Compounds Np₃M, Am₃M, and on the System Pu-Am

A. L. Kutepov

October 4, 2005

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

LIMITED LIABILITY COMPANY "STRELA"

REPORT

MATERIAL SUPPORT AGREEMENT No. B541413

Deliverable 2. Tasks 2.1-2.4

**CALCULATIONAL STUDY ON THE COMPOUNDS Np_3M , Am_3M , AND ON
THE SYSTEM Pu-Am**

Principal Investigator



A. L. Kutepov

Snezhinsk-2005

This work was funded under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Abstract

Spin-polarized relativistic density functional theory has been employed for the study of the electronic and magnetic structures for the compounds Np_3M and Am_3M ($M = Al, Ga, In$) and their comparison with plutonium's alloys Pu_3M has been made. It has been found that of the three actinides (Np, Pu, Am) only plutonium has its FCC structure essentially more stable after alloying with aforementioned elements. Apart from that, the electronic and magnetic structures for the system Pu-Am presented by three different compounds: Pu_3Am , $PuAm$, and $PuAm_3$ have been investigated. Their magnetic structures have been found to be too robust in comparison with the experimental fact that magnetism in Pu-Am system depends strongly on the percentage of the americium in the alloy. One possible explanation consists in the overestimation of the spin splitting and in the disregarding of orbital dependance of the exchange-correlation potential.

I. INTRODUCTION

Previous report was mainly dedicated to the studying of plutonium's compounds Pu_3M ($M = Al, Ga, In$). The metals Al , Ga , and In are known to be the stabilizing elements for δ -Pu, i.e. small amounts of them used as alloying elements can stabilize δ -Pu down to about room temperatures. From theoretical points of view the explanation of the stabilization appeared to be possible only in the calculations with the spin-polarization included. The explanation is thus as follows: Due to the interference of spin-orbit interaction and exchange splitting the bottom of plutonium's $5f$ states is shifted to the lower energies as compared with the results from non-magnetic calculations. This circumstance leads to the stronger hybridization between Pu $5f$ and p -levels of alloying metal which in turn increases the binding energy and can be considered as a main reason for the stabilization.

The question addressed in the present report is whether fcc Pu is the only actinide which becomes more stable with the small additions of the above mentioned metals or its neighbors (Np and Am) also possess of such peculiarity. Thus, keeping this question in mind, the formation energies, electronic and magnetic structures for the compounds Np_3M and Am_3M ($M = Al, Ga, In$) have been calculated.

Another objects addressed in this report are the following compounds of Pu and Am: Pu_3Am , $PuAm$, and $PuAm_3$. These compounds are interesting due to the discovery of Curie-Weiss behavior of the magnetic susceptibility in the Pu-Am system with concentration of Am about 24% and more, [1]. So, it is interesting to know what is happening with the electronic and magnetic structures when one is passing from δ -Pu to Am. The alloys of Pu and Am have already been studied by Landa and Söderlind, [2], with scalar-relativistic spin-polarized FPLMTO method, [3,4], and KKR-ASA method, [5,6]. They have addressed the questions of crystal stability and electronic structure for Pu-Am system with Am concentration up to 30%. The authors of [2] have calculated the paramagnetic \rightarrow antiferromagnetic transition temperature (T_c) of $Pu_{1-x}Am_x$ alloys by the Monte Carlo technique and have found that by introducing Am into the system one could lower T_c from ~ 548 K (pure Pu) to 372K ($Pu_{0.7}Am_{0.3}$).

In the present work the electronic and magnetic structure of the system Pu-Am has been investigated as a function of the Am concentration and the fully relativistic approach has been used for it.

The report is organized as follows. In section II the computational method and its parameters are described briefly. The results obtained for the compounds Np_3M and Am_3M ($M = Al, Ga, In$) are discussed and their comparison with Pu_3M is given in the section III. In the section IV the results of studying upon $Pu - Am$ system are given. Lastly, in section V the conclusions and future plans are offered.

II. DETAILS OF CALCULATIONS

The density functional theory in the generalized gradient approximation, [7], has been employed in this work. The calculations have been performed with the full potential, Dirac relativistic (j, κ) basis, spin-polarized linear-augmented-plane-wave method (RSPFLAPW+LO). The details of the method were presented earlier, [8].

All calculations for the compounds A_3M ($A = Np, Am; M = Al, Ga, In$) have been carried out with cubic $AuCu_3$ structure. The compounds Pu_3Am and $PuAm_3$ were also treated in this crystal structure. For antiferromagnetic calculations on $PuAm$ a four-atom cell was applied (original four-atom cell of fcc -structure with 2 Pu atoms replaced with Am atoms). Theoretical volumes which were found by minimizing the total energy were used in our study. In the Table I these volumes are listed for the references.

Within the muffin-tin spheres the charge density and potential have been expanded in spherical harmonics with a cutoff L_{max} equal to 6. The angular momentum cutoff $L_{max} = 10$ has been used for the basis functions. The basis set has also included the semicore orbitals - $5d, 6s$ and $6p$ for actinides. The plane wave expansion of the wave functions has been terminated in such a manner that the convergence of the total energy was better than 1 mRy per atom in all the cases.

TABLE I: Equilibrium volumes for the compounds of actinides (a.u./atom) from nonmagnetic (NM) and magnetic (M) calculations.

Compound	NM	M	Compound	NM	M	Compound	M
Np_3Al	129.3	138.4	Am_3Al	129.6	181.3	Pu_3Am	154.4
Np_3Ga	128.4	139.0	Am_3Ga	137.7	178.2	$PuAm$	175.5
Np_3In	146.1	170.1	Am_3In	159.7	198.0	$PuAm_3$	185.3

The integration over Brillouin zone has been carried out by the improved tetrahedron method, [9]. 294 irreducible \mathbf{k} -points have been used in all self-consistent calculations on the compounds with $AuCu_3$ structure. 216 irreducible points has been used for $PuAm$.

III. THE RESULTS OF STUDYING ON Np_3M AND Am_3M ($M = Al, Ga, In$). COMPARATIVE ANALYSIS OF ACTINIDES COMPOUNDS Np_3M , Pu_3M , AND Am_3M .

A. Formation energies

As a first step, the energies of formation have been calculated for the compounds A_3M . Non-spin-polarized and spin-polarized calculations have been performed. As antiferromagnetic configurations are difficult to generate in complex alloy structure, the ferromagnetic ordering was used in the spin-polarized calculations. The formation energies have been found via the relation [10]

$$E_{A_{1-x}M_x}^f = E_{A_{1-x}M_x} - ((1-x)E_A + xE_M) \quad (1)$$

The results have been collected in the Table II. If we compare these results with the results for Pu_3M (Table I in the previous report) we will see that the addition of alloying elements has much more prominent effect on stabilization of Pu than on stabilization of its neighbors Np and Am. Indeed, it is seen from the calculations that the compounds Am_3M are not stable at all, and only Np_3Al and Np_3Ga are stable in the case of Np. It is interesting also that for Am_3Al and Am_3Ga the effect of spin-polarization is opposite to the effect for another compounds (in the spin-polarized calculations the stability of Am_3Al and Am_3Ga is even less than in the non-spin-polarized calculations). This may be correlated with the fact that the atomic volumes (Table I) in the compounds Am_3Al and Am_3Ga are smaller

TABLE II: Formation energies for compounds A_3M ($A = Np, Am, M = Al, Ga, In$)(in eV/atom) from nonmagnetic (NM) and ferromagnetic (FM) calculations.

	Np_3Al	Np_3Ga	Np_3In	Am_3Al	Am_3Ga	Am_3In
NM	-0.035	-0.077	0.248	0.128	0.021	0.292
FM	-0.077	-0.124	0.051	0.217	0.085	0.084

TABLE III: The atomic magnetic moments (in Bohr’s magnetons) on the actinides atoms in the neptunium’s and americium’s compounds.

Compound	Atom	M_{spin}	M_{orb}	M_{total}
Np_3Al	Np	2.170	-1.539	0.631
Np_3Ga	Np	2.333	-1.650	0.683
Np_3In	Np	3.562	-2.616	0.946
Am_3Al	Am	6.513	-0.557	5.956
Am_3Ga	Am	6.528	-0.549	5.979
Am_3In	Am	6.477	-0.562	5.915

than in pure Am.

B. Electronic and magnetic structure

The partial DOSs for the compounds A_3M are presented in the Figures 1 and 2. Total densities of states are given in the Figures 3 and 4. Calculated magnetic moments have been placed in the Table III. The spin-resolved DOSs (differential with respect to energy magnetic moments) are presented in the Figure 5. Also, in these figures the so called magnetic-moment functions are presented. The magnetic-moment function is the contribution to the total moment ($M_{spin} + M_{orb}$) from one-particle states integrated up to the given energy. So, the magnetic-moment function can be considered as some generalization of the definition of atomic magnetic moment, the latter just being the value of the above function at the Fermi energy.

Looking on the Fig. 2 and on the Fig. 1-3 in the previous report it is easily to see that relative shifting is happening between $5f_{5/2}$ states of actinide element and p -states of alloying element when we are going from Np to Am. This shifting imposes an interesting consequence for the stability of these compounds, as it is explained further.

Obviously, the origin of stability (or its absence) should be looking for in the hybridization between the states of actinide metal and the states of alloying element. As we can see from the Figures 1-3 (previous report), the group of plutonium’s $5f_{5/2}$ states situated between -1.5eV and -0.5eV takes the same position as the main part of p -states of alloying element

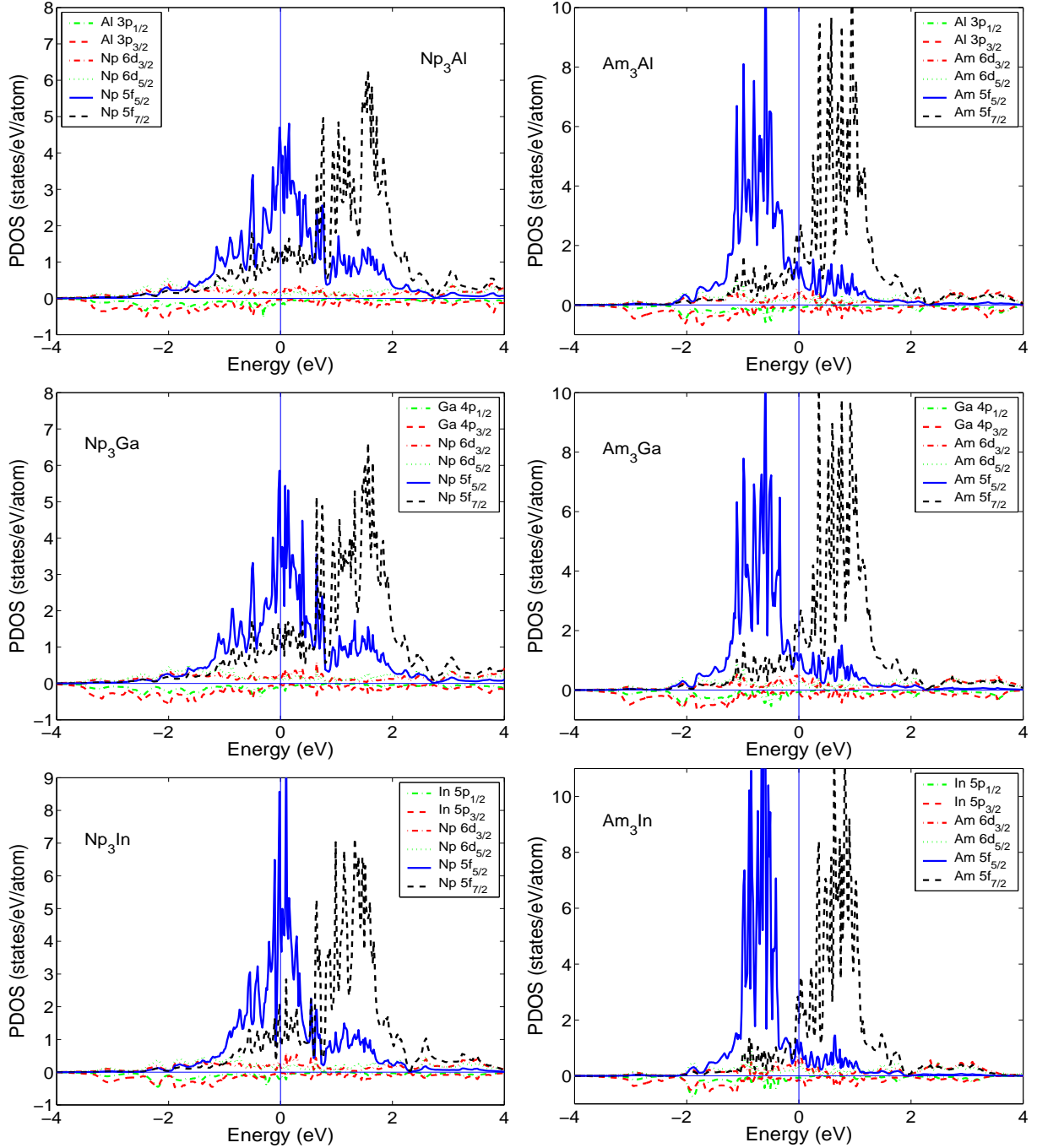


FIG. 1: Partial densities of states (PDOS) for the compounds A_3M ($A = Np, Am$ and $M = Al, Ga, In$) from nonmagnetic calculations. Fermi level is shifted to zero energy. The states of M are given with negative sign for convenience.

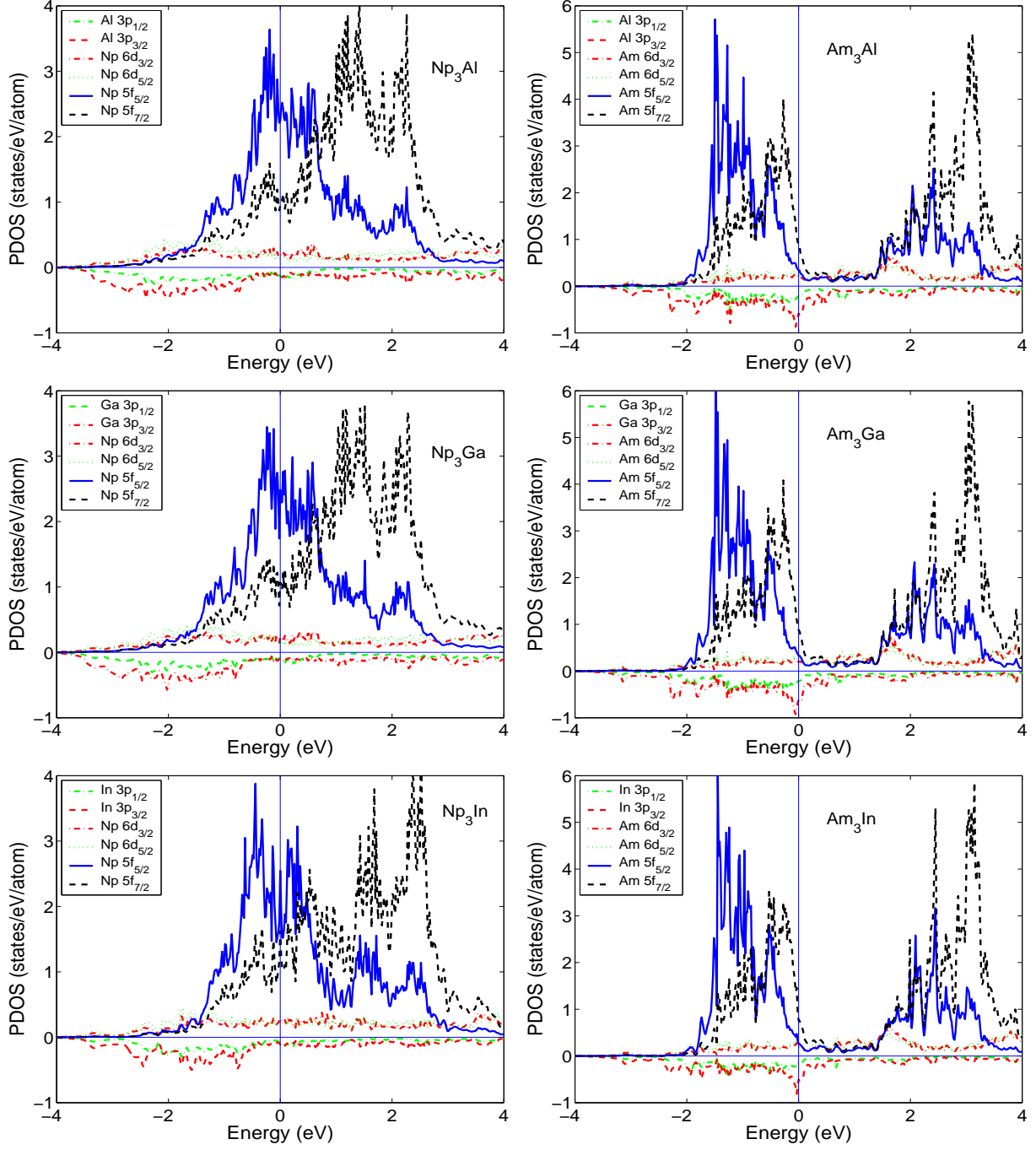


FIG. 2: Partial densities of states (PDOS) for the compounds A_3M ($A = Np, Am$ and $M = Al, Ga, In$) from ferromagnetic calculations. Fermi level is shifted to zero energy. The states of M are given with negative sign for convenience.

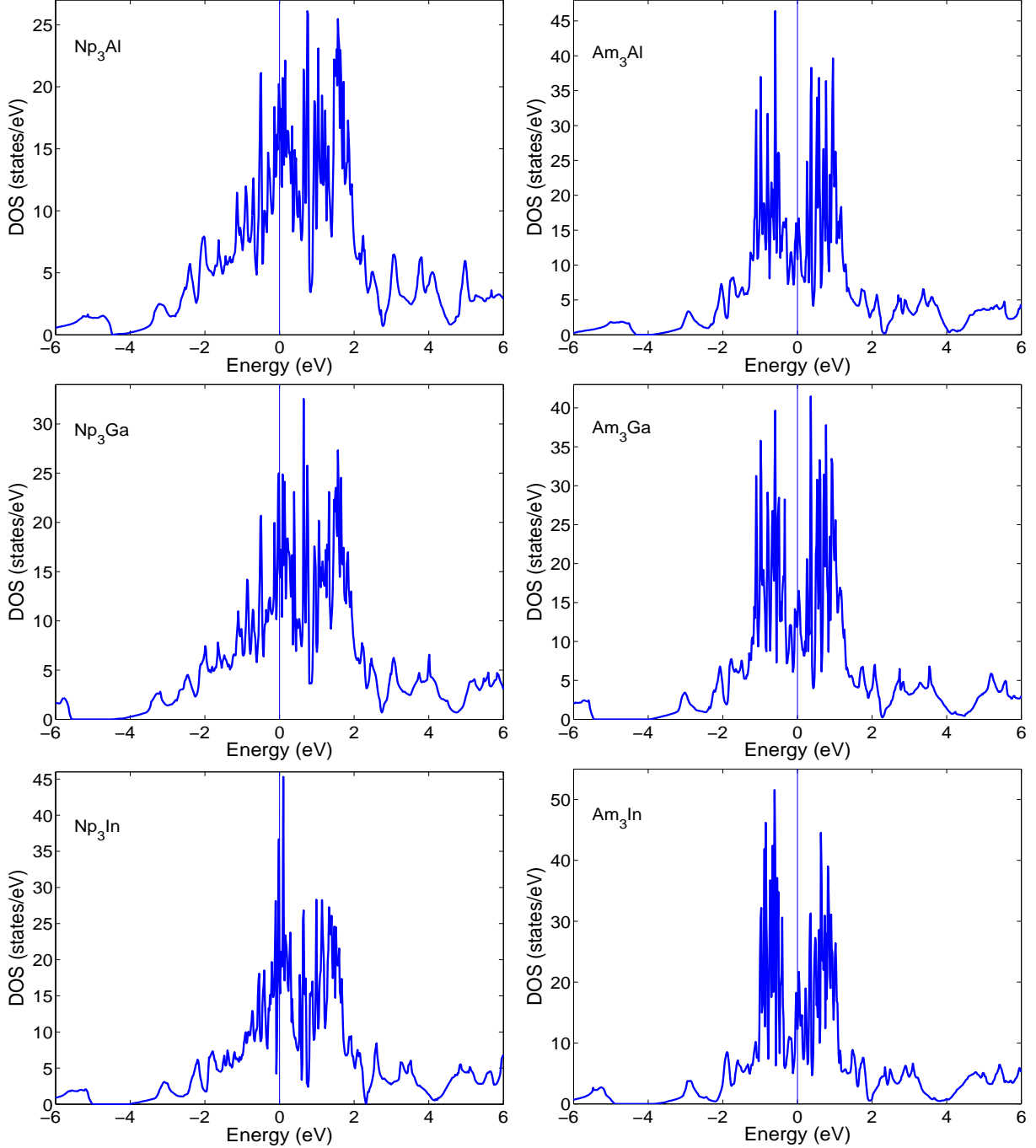


FIG. 3: Total densities of states (DOS) for compounds Np_3M and Am_3M from nonmagnetic calculations. Fermi level is shifted to zero energy.

does. So, we have strong hybridization in the Pu_3M compounds and high level of stability of them. If we look, however, at the Figures 2 (present report) we will see that main part of p -states of foreign element is shifted down relative to actinide's $5f_{5/2}$ states for Np compounds and is shifted up for Am compounds. Thus, in both cases the hybridization is diminished

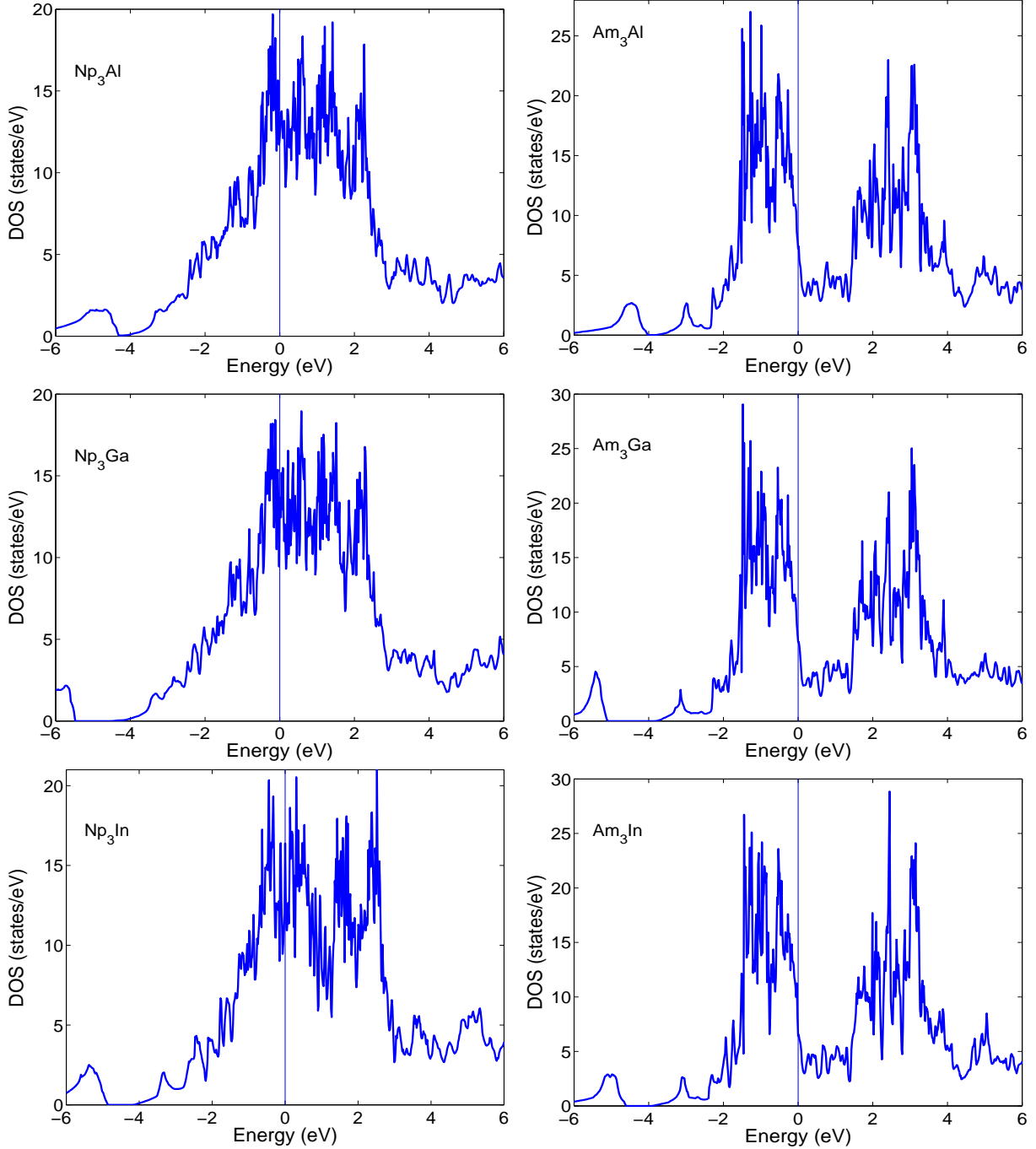


FIG. 4: Total densities of states (DOS) for compounds Np_3M and Am_3M from ferromagnetic calculations. Fermi level is shifted to zero energy.

resulting in small (though negative) formation energies for Np compounds and in positive energies of formation for Am compounds.

Let us now consider spin-resolved DOSs and magnetic-moment functions (Figure 5 of the present report and Figures 5,6 of the previous report). We can see that all compounds have

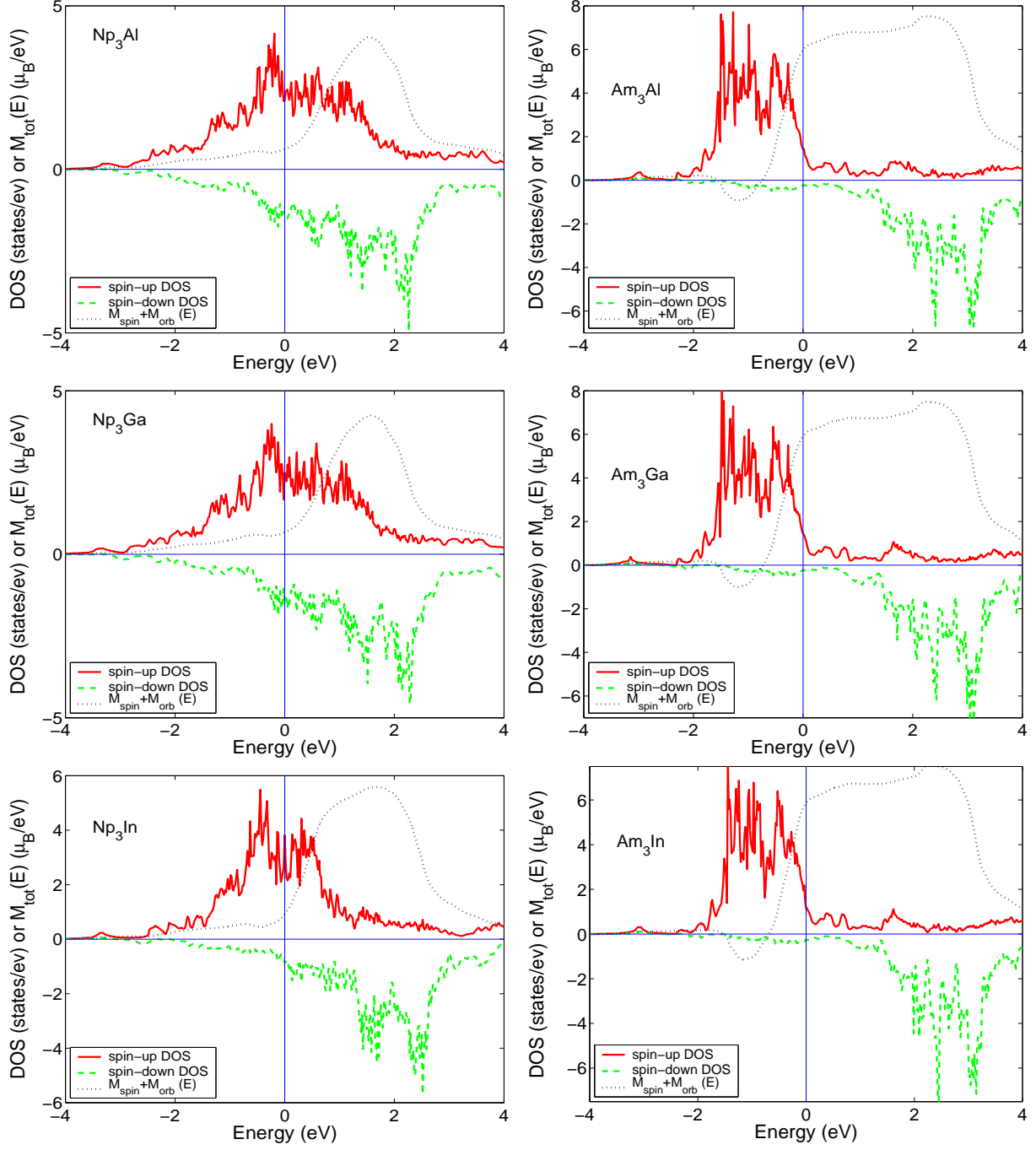


FIG. 5: Spin-resolved DOS and magnetic-moment function (see text for the explanation) for Np and Am atoms in the compounds A_3M ($A = Np, Am$ and $M = Al, Ga, In$). Fermi level is shifted to zero energy. Spin-down DOS is shown with negative sign.

TABLE IV: The atomic magnetic moments (in Bohr’s magnetons) on the actinides atoms in the Pu-Am compounds.

Compound	Atom	M_{spin}	M_{orb}	M_{total}
<i>Pu₃Am</i>	Pu	4.400	-1.949	2.451
	Am	5.692	-0.612	5.080
<i>PuAm</i>	Pu	4.625	-2.204	2.421
	Am	5.924	-0.687	5.237
<i>PuAm₃</i>	Pu	4.713	-2.580	2.133
	Am	6.093	-0.770	5.323

some magnetic structure (spin-up and spin-down densities of states are shifted relatively of each other and, also, Table III show us the big spin moments on the atoms). But if we look at the magnetic-moment functions, we can see that in the neptunium’s compounds this function has small value at E_f and, so, the the total moment is close to zero (due to the cancellation between spin and orbital moments). Further, for Pu compounds the magnetic-moment function intersects E_f at its slope and for Am compounds the intersection takes place at the beginning of saturation of the total moment.

Thus, this consideration clearly places Pu (from density-functional point of view) between two types of actinide metals - light, with zero (or almost zero) total moments and heavy with big total moments.

IV. *PuAm*: MAGNETIC STRUCTURE, TOTAL AND PARTIAL DOS

In the present report the investigation on the compounds of Pu with its neighbors in the Periodic Table has been continued by studying on Pu-Am system. As it was found in the calculations in the previous report, the formation energy of PuNp is positive, i.e. pure Pu and Np are more stable than their compound. As to Pu-Am system, in the present report three compounds of Pu with Am (*Pu₃Am*, *PuAm*, and *PuAm₃*) have been investigated and the following formation energies have been found: -0.134eV/atom for *Pu₃Am*, -0.128eV/atom for *PuAm*, and -0.055eV/atom for *PuAm₃*. Thus, these calculations confirm the experimental fact, that Am stabilizes δ -Pu.

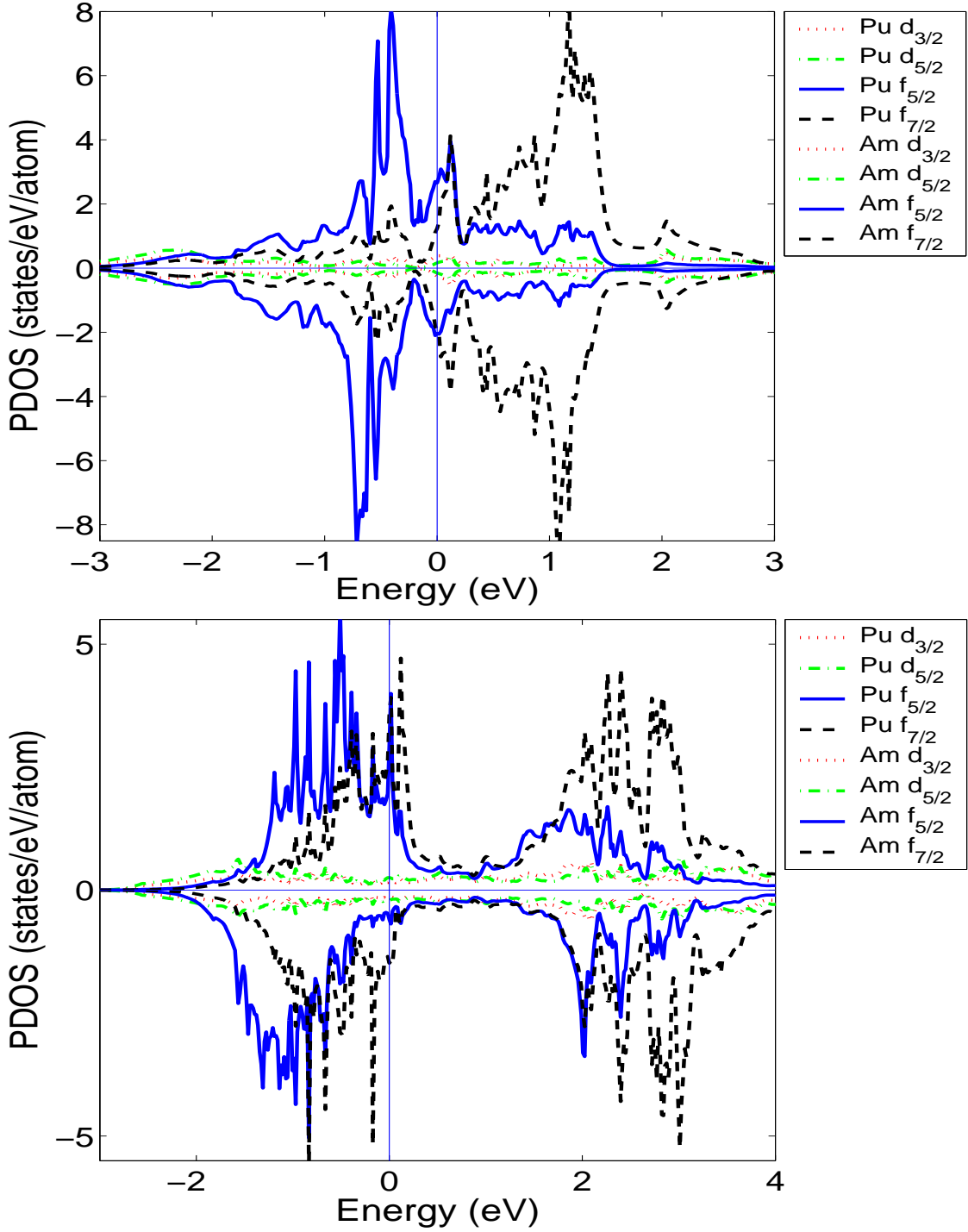


FIG. 6: Partial densities of states (PDOS, states/eV) for nonmagnetic (upper panel) and ferromagnetic (lower panel) $PuAm$. Fermi level is shifted to zero energy. The states of Am are given with negative sign for convenience.

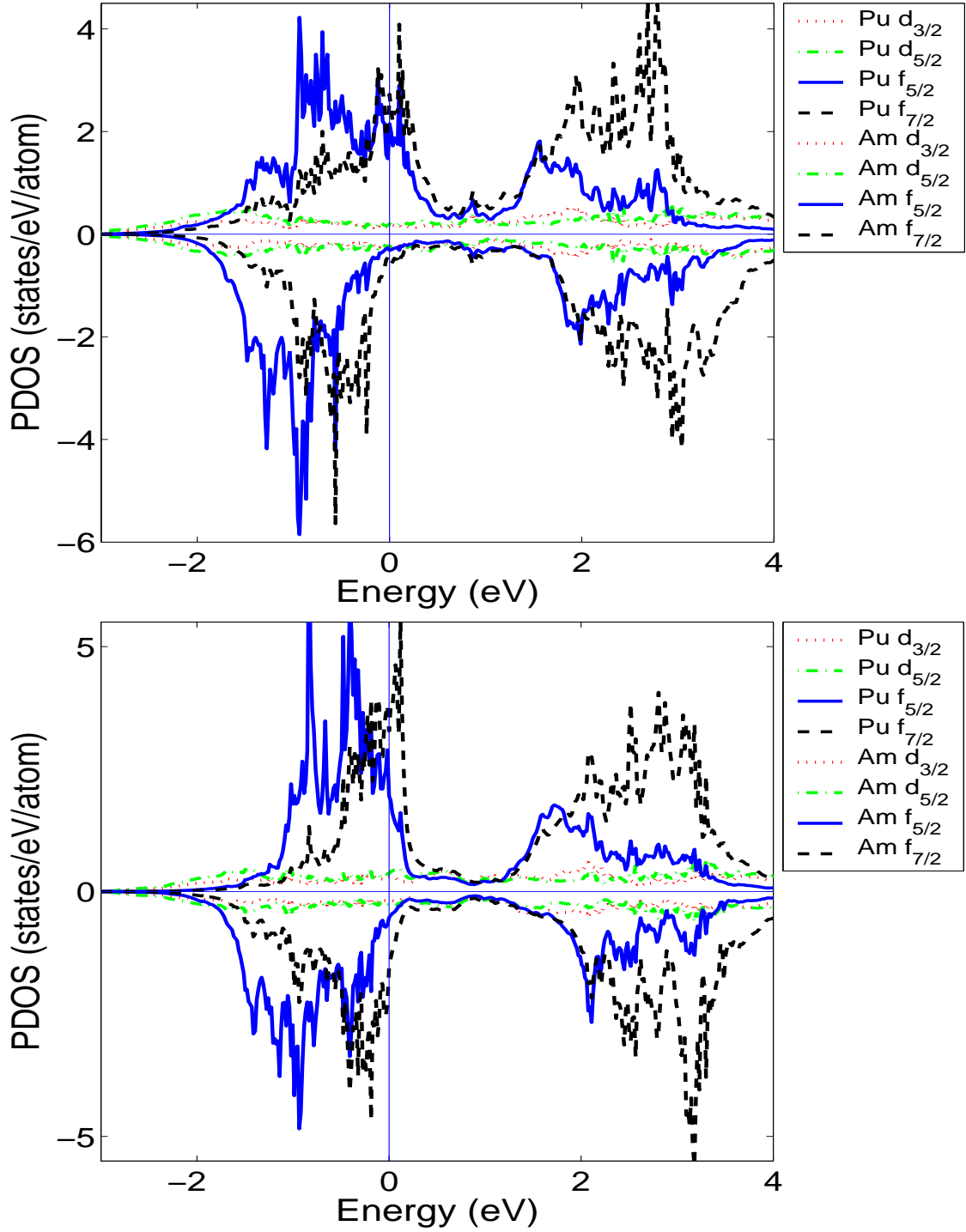


FIG. 7: Partial densities of states (PDOS, states/eV) for ferromagnetic Pu_3Am (upper panel) and $PuAm_3$ (lower panel). Fermi level is shifted to zero energy. The states of Am are given with negative sign for convenience.

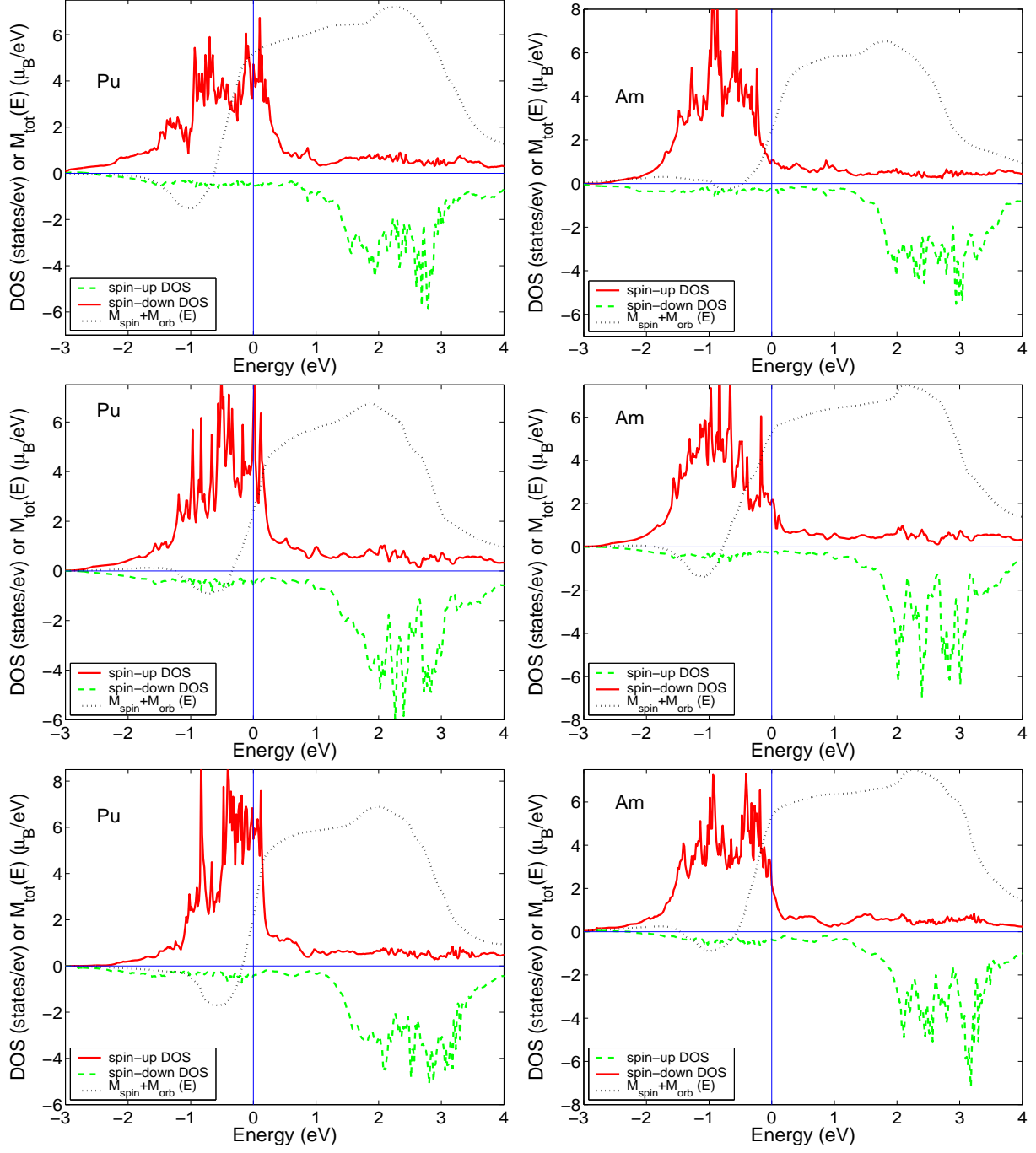


FIG. 8: Spin-resolved DOS and magnetic-moment function (see Section III B for the explanation) for Pu and Am atoms in the compounds Pu_3Am (upper row), $PuAm$ (middle row), and $PuAm_3$ (lower row). Fermi level is shifted to zero energy. Spin-down DOS is shown with negative sign.

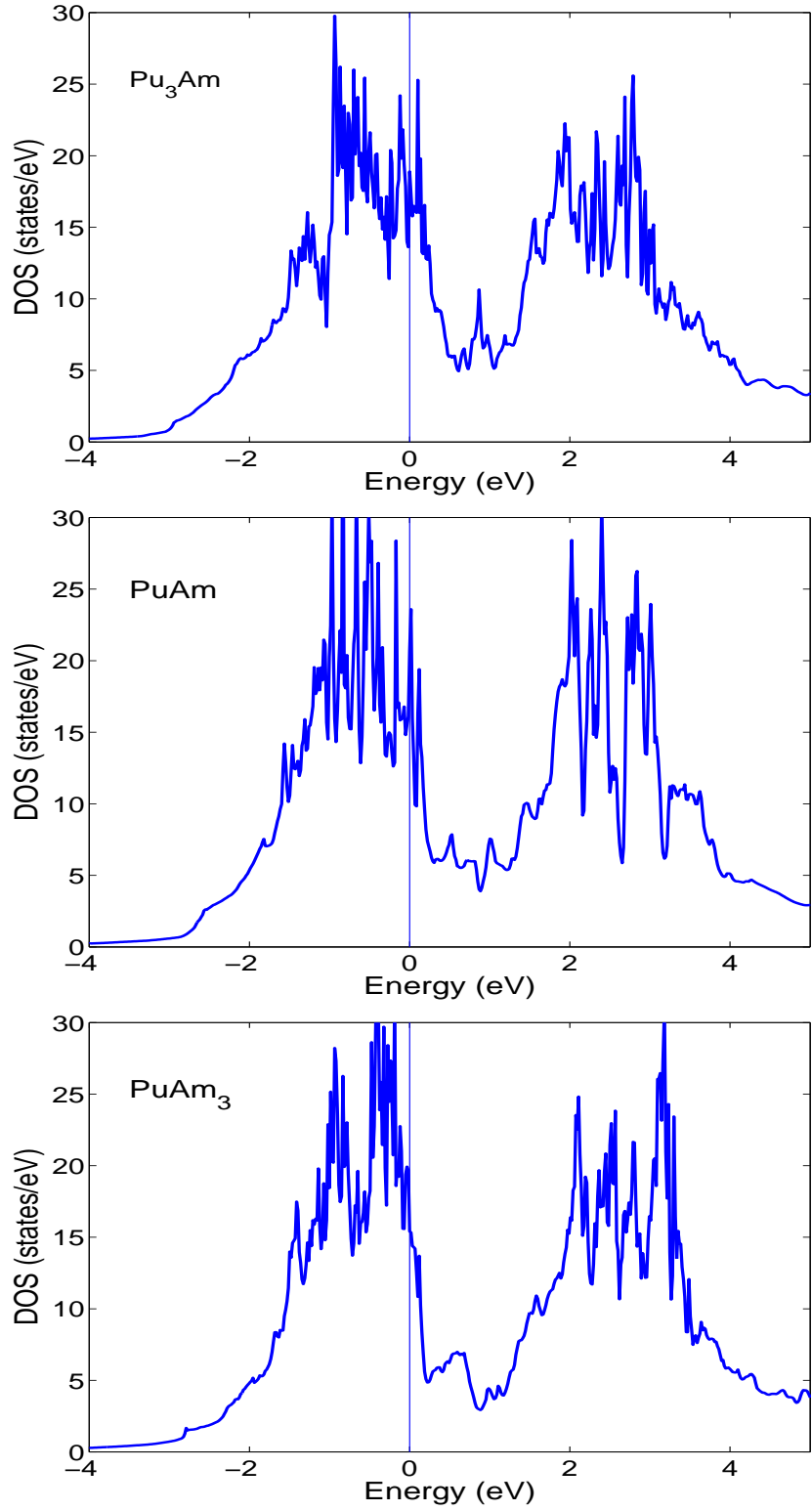


FIG. 9: Total densities of states (DOS, states/eV) for the compounds Pu_3Am , $PuAm$, and $PuAm_3$ from antiferromagnetic calculations. Fermi level is shifted to zero energy.

The electronic (partial DOS) and magnetic (spin-resolved DOS) structures are presented in the Figures 6-7 and 8 correspondingly. Total DOS is given in the Figure 9. Calculated magnetic moments for spin-polarized case are given in the Table IV.

The most striking result for us is that the electronic structure and magnetic behavior of the Pu and Am atoms in the compounds are not very much different from the electronic and magnetic structures of pure Pu and Am (see previous report for pure actinides) though, having in mind the experimentally discovered magnetism in $Pu_{1-x}Am_x$ ($x \sim 0.24$), [1], we had expected some difference for, at least, the compound Pu_3Am . This similarity then makes us think that our calculations bring to the electronic structure which is too robust. The reason, apparently, is the overestimation of the spin separation between two lobes of the states. It is seen from the Fig. 8: the low-energy lobe consist almost completely of the spin-up states for both Pu and Am, and Fermi energy cuts 5 electrons from this manifold for Pu and 6 electrons for Am giving the big spin moments. Apparently, the origin of these drawbacks should be sought in the approximate form of exchange-correlation functional: we obtain the exchange-correlation potential varying only spin part of magnetization density. This approach for the systems with big orbital moments (like Pu) (orbital moments are calculated at this level of theory!) may lead, beyond any doubt, to the wrong results.

V. CONCLUSIONS AND PLANS FOR THE FUTURE

In summary, first-principles relativistic GGA-based calculations have been applied to describe the electronic and magnetic structure for the compounds Np_3M and Am_3M ($M = Al, Ga, In$) and to find their formation energies. The comparative analysis of the compounds of actinides with Al, Ga, and In has been performed based on their electronic and magnetic structure.

Apart from that, the electronic and magnetic structures for the system Pu-Am presented by three different compounds: Pu_3Am , $PuAm$, and $PuAm_3$ have been investigated. Despite the reasonable description of the volumes, one serious defect was discovered during this study: the experimental fact consisting in sensitivity of magnetic structure of Pu-Am system has not been confirmed in the calculations. Probably, the reason of that is in the overestimation of the spin splitting and in the disregarding of orbital dependance of the exchange-correlation potential. This drawback might be cured with methods which take

orbital dependance of the potential into consideration explicitly and without any approximations. So, future plan may consist in developing of a relativistic variant of crystalline Hartree-Fock method - Dirac-Hartree-Fock approach for the solids and in using it for the studying of actinides. We hope, that if the problem consists of the neglecting of orbital degrees of freedom, it will be solved with success.

- ¹ M. Dorneval, Electronic structure of Pu-Ce(-Ga) and Pu-Am(-Ga) alloys stabilized in the δ -phase. Ph.D. Thesis, Universite de Bourgogne, Dijon, France, 2001.
- ² A. Landa and P. Söderlind, *J. of Alloys Comp.* **376**, 62 (2004).
- ³ J. M. Wills and B. R. Cooper, *Phys. Rev. B* **36**, 3809 (1987).
- ⁴ D. L. Price and B. R. Cooper, *Phys. Rev. B* **39**, 4945 (1989).
- ⁵ I. A. Abrikosov and H. L. Skriver, *Phys. Rev. B* **47**, 16532 (1993).
- ⁶ A. V. Ruban and H. L. Skriver, *Comput. Mater. Sci.* **15**, 119 (1999).
- ⁷ J. Perdew, S. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁸ A. L. Kutepov and S. G. Kutepova, *J. Phys.: Condens. Matter* **15**, 1 (2003).
- ⁹ P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- ¹⁰ G. Robert, A. Pasturel, and B. Siberchicot, *Phys. Rev. B* **68**, 075109 (2003).