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THEORETICAL STUDY ON THE COMPOUNDS NpM_2, PuM_2, AmM_2 (M = Mn, Fe, Ni, Co) AND ON THE SYSTEM Pu-U.

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Abstract

The relativistic spin-polarized density functional theory has been used for the study of electronic and magnetic structure of the compounds NpM_2, PuM_2 and AmM_2 $(M = Mn, Fe, Co, Ni)$. It has been shown that the peculiarities in their magnetic properties come mainly from the hybridization between 5f-electrons of actinides and 3d-electrons of transition metals. It is interesting, that existence of the local magnetic moments appears to be possible on the atoms, despite the fact that Hill's condition is not satisfied for these compounds of actinides. Besides, the electronic and magnetic structures of PuU have been studied and the comparative analysis of them with another compounds of plutonium and its neighbors in Periodic System: PuNp and PuAm has been performed. It has been found that in all the cases the electronic structure formation is a result of a superposition of spin-orbit and exchange band splitting with some increasing of the role of exchange as we are going to americium. Atoms of plutonium appear to be near the point of equal importance of both interactions.

I. INTRODUCTION

The key circumstance, which defines the magnetic properties of actinides as well as their compounds, is the degree of localization of 5f-electrons. The localization, in turns, depends mainly on the distance d_A between the nearest atoms of actinides in the crystal, more exactly, on the relation of average radius $\langle r_{5f} \rangle$ of 5f-shell of actinide and half of the distance between the nearest atoms of actinide. The first, who turned in 1970 the attention on the dependence of the magnetic properties of actinides compounds on the interatomic distance d_A was H.Hill, [1]. He generalized and systematized the data known by that time on the magnetic characteristics of the compounds of uranium, neptunium, and plutonium. From his supervision Hill made the conclusion that, as a rule, the magnetic order exists in those compounds, in which the distance d_A exceeds some critical value d_k (for the uranium compounds $d_k \approx 3.5\AA$). In the compounds with $d_A < d_k$ there is Pauli paramagnetism weakly dependant on the temperature and superconductivity. The analogous correlation between magnetic properties and the interactinide distance has also been found in neptunium's ($d_k \approx 3.2\AA$) and plutonium's ($d_k \approx 3.4\AA$) compounds. This correlation is present also in the compounds of one of the rare earth elements - cerium. The existence of some critical distance d_k on the Hill's diagrams, as well as the presence of sharp border between actinides with delocalized and with localized 5f-electrons, can be explained in terms of Mott's transition. This transition is also an origin of a tendency to the magnetic ordering at $d_A > d_k$. Thus, the Hill's diagrams tell us that the behavior of 5f-electrons in the compounds of actinides is defined mainly by the degree of overlap between their wave functions, which, in turns, depends firstly on the geometric factors. The chemical environment plays no definitive role, but sometimes its influence leads to the exceptions from the Hill's rule. A few of such exceptions are found among the intermetallic compounds of actinides and "magnetic" 3d-metals - manganese, iron, cobalt, and nickel. In these compounds the interactinide distance $d_A < d_k$, but many of them have magnetic order, though there is no any simple law of changing of their properties with changing of d_A. The cause of such a situation is, obviously, that 5f-electrons of actinides hybridize with 3d-electrons of transition metals, i.e. it seems that the peculiarities of the properties of these compounds are the results of a complex behavior of the density of states near Fermi level. Thus, it is interesting to study the details of the electronic structure of these intermetallic compounds from the point of view of ab-initio calculations, with the purpose of answering the question of the causes of such peculiar magnetic behavior of them. To this aim the present work has mainly been intended.

Another object, which has been investigated in the present work, is the compound PuU. The studying of it was the prolongation of the investigation of the compounds of plutonium with its neighbors Np and Am with the purpose to discover some tendencies in changing of the properties and to understand better the properties of plutonium itself.

The preprint is organized as follows. In the chapter II the calculational method and parameters used are described. The results obtained for the compounds NpM_2, PuM_2, and AmM_2 ($M = Mn, Fe, Co, Ni$) are discussed in the chapter III. Further, in chapter IV the calculations for PuU are given and the comparison with PuNp and PuAm is carried out.

II. THE DETAILS OF THE CALCULATIONS

Density functional theory in generalized gradient approximation, [3], has been used in all calculations of the present work. As a computer code we have used the full-potential, relativistic spin-polarized linear method of augmented plane waves (RSPFLAPW+LO). The formulas of this method had been given earlier, [4].

All studies for the compounds AM_2 ($A = Np, Pu, Am$; $M = Mn, Fe, Co, Ni$) have been performed with cubic crystal structure of $MgCu_2$ type, [2]. Electronic structure has been obtained for the theoretical equilibrium volumes, which have been found by minimizing the total energy as a function of volume. The corresponding theoretical interactinide distances are given in the Table I for the purposes of reference. The fcc-lattice doubled in z-direction has been used for PuU.

TABLE I: Calculated equilibrium distances between atoms of actinide (Å) for the compounds AM_2 ($A = Np, Pu, Am$, $M = Mn, Fe, Co, Ni$). Experimental data, [2], are given in parentheses for the purpose of comparison.

	Mn	Fe	Co	Ni
Np	3.11(3.13)	3.10(3.09)	3.06(3.045)	3.10(3.075)
Pu	3.14(3.15)	3.13(3.11)	3.08(3.07)	3.11(3.09)
Am	3.20	3.13	3.15	3.16

Inside muffin-tin spheres the electronic density and potential were expanded in spherical harmonics up to L_{max}, equal 6. The maximum value of angular moment $L_{max} = 10$ was used for the expansion of basis functions. Basis set also included the semicore orbitals - $5d, 6s$, and $6p$ for actinides. Plane wave expansion of basis functions in interstitial region was controlled by the condition of total energy convergence to be better than 1 mRy per atom.

The integration over Brillouin zone was carried out with improved tetrahedron method, [5]. 90 irreducible **k**-points were used in the calculations of crystals with $MgCu_2$ structure. 476 irreducible points were used in the case of PuU.

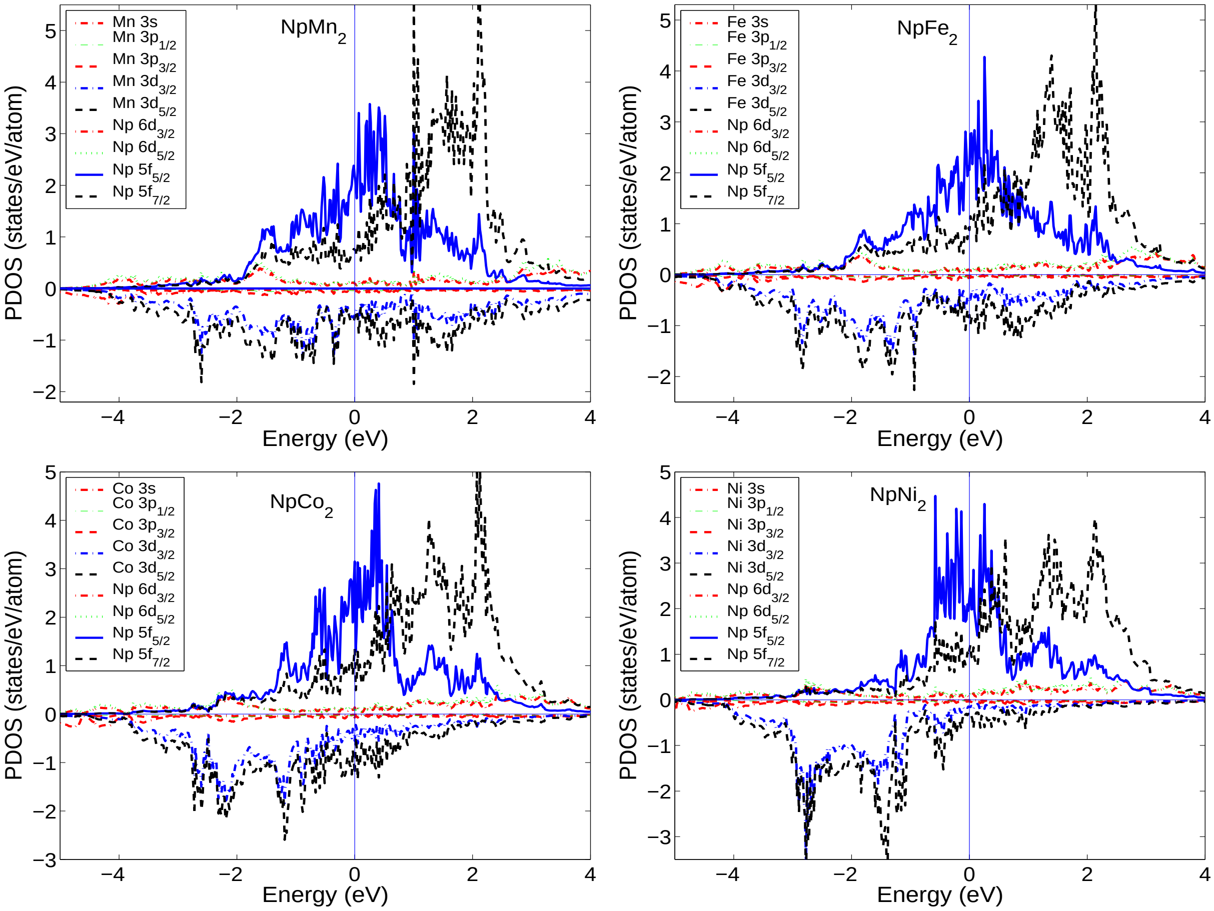

FIG. 1: Partial densities of states for the compounds NpM_2 ($M = Mn, Fe, Co, Ni$) from spin-polarized calculations. Fermi level is taken as zero energy. The DOS for M are given with negative sign for the convenience of viewing.

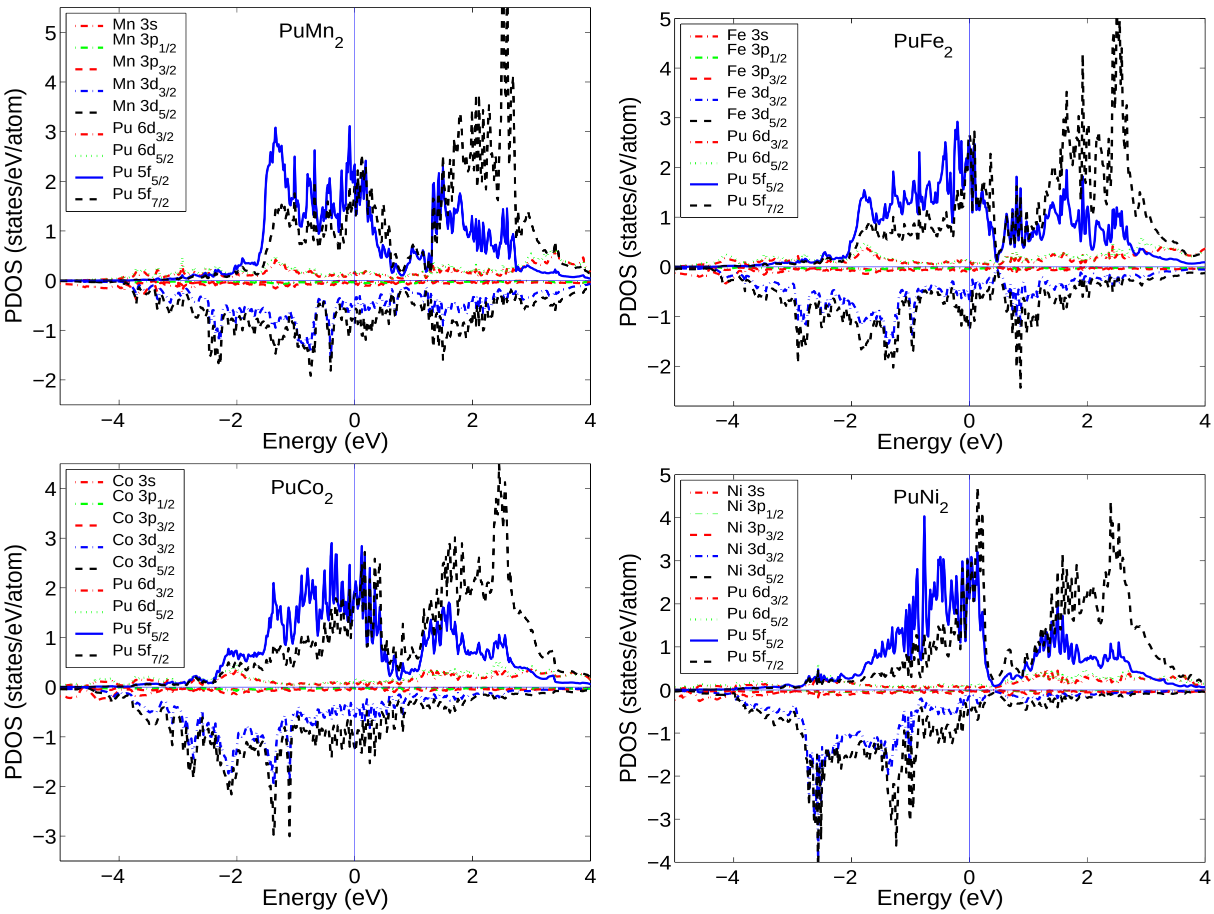

FIG. 2: Partial densities of states for the compounds PuM_2 ($M = Mn, Fe, Co, Ni$) from spin-polarized calculations. Fermi level is taken as zero energy. The DOS for M are given with negative sign for the convenience of viewing.

III. THE RESULTS OF STUDYING OF THE COMPOUNDS AM_2 ($A = Np, Pu, Am$; $M = Mn, Fe, Co, Ni$).

As it is seen from the Table I, the calculated distances between the atoms of actinides (and, therefore, equilibrium volumes) are rather close to their experimental values. Besides, the general tendency of the experimental results is reproduced properly: either for neptunium or for plutonium, the largest interatomic distance is for their compounds with manganese, and the smallest distance - for compounds with cobalt. This circumstance let us study the electronic structure with more confidence.

The calculated results on the electronic and magnetic structure are presented in the Figures 1- 3 (partial densities of states), 7- 9 (total densities of states), 4- 6 (spin-resolved

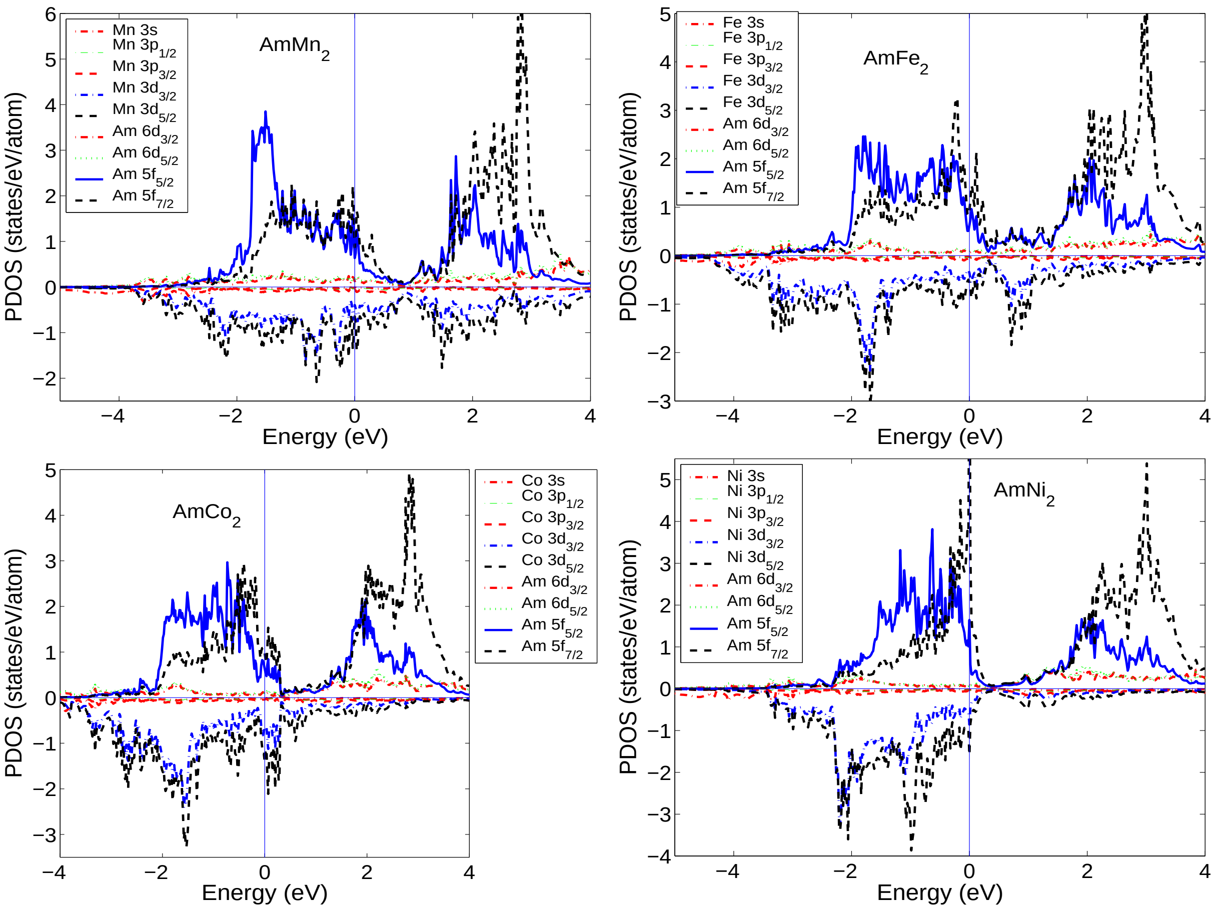

FIG. 3: Partial densities of states for the compounds AmM_2 ($M = Mn, Fe, Co, Ni$) from spin-polarized calculations. Fermi level is taken as zero energy. The DOS for M are given with negative sign for the convenience of viewing.

densities of states) and in the Table II (orbital, spin and total magnetic moments). Also, in the Figures 4- 6, 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.

First, let us consider the calculated magnetic moments. Comparing the calculated values of the total magnetic moment per formula unit with their experimental values (we know measurements only for neptunium's and plutonium's compounds), we can note the good agreement of magnetization for the compounds of Np (excluding $NpMn_2$). For the compounds of Pu the satisfactory agreement has been obtained only in the case of $PuFe_2$. We

TABLE II: Atomic magnetic moments (Bohr's magnetons) of actinides in the compounds of neptunium, plutonium, and americium. Also, the total moments on the formula unit are given in comparison with the existing experimental data, [2].

Compound	Atom	M_{spin}	M_{orb}	M_{total}	—$M^{theor}_{formula}$—	—$M^{exp}_{formula}$—
$NpMn_2$	Np	2.73	−1.56	1.17	2.21	0.4
	Mn	−1.89	−0.30	−2.19		
$NpFe_2$	Np	3.10	−2.03	1.07	2.55	2.6
	Fe	−1.69	−0.12	−1.81		
$NpCo_2$	Np	3.05	−2.11	0.94	0.54	1.0
	Co	−0.70	−0.04	−0.74		
$NpNi_2$	Np	3.18	−2.50	0.68	0.84	1.0
	Ni	0.06	0.02	0.08		
$PuMn_2$	Pu	4.69	−2.18	2.51	2.11	-
	Mn	−2.26	−0.05	−2.31		
$PuFe_2$	Pu	4.58	−2.14	2.44	1.40	2.27
	Fe	−1.88	−0.04	−1.92		
$PuCo_2$	Pu	4.57	−2.06	2.51	0.37	-
	Co	−1.05	−0.02	−1.07		
$PuNi_2$	Pu	4.49	−2.33	2.16	2.24	-
	Ni	0.00	0.04	0.04		
$AmMn_2$	Am	5.94	−0.99	4.95	0.55	?
	Mn	−2.20	0.00	−2.20		
$AmFe_2$	Am	5.86	−1.18	4.68	0.68	?
	Fe	−2.00	0.00	−2.00		
$AmCo_2$	Am	6.12	−0.86	5.26	2.38	?
	Co	−1.35	−0.09	−1.44		
$AmNi_2$	Am	6.01	−0.94	5.07	4.85	?
	Ni	−0.11	0.00	−0.11		

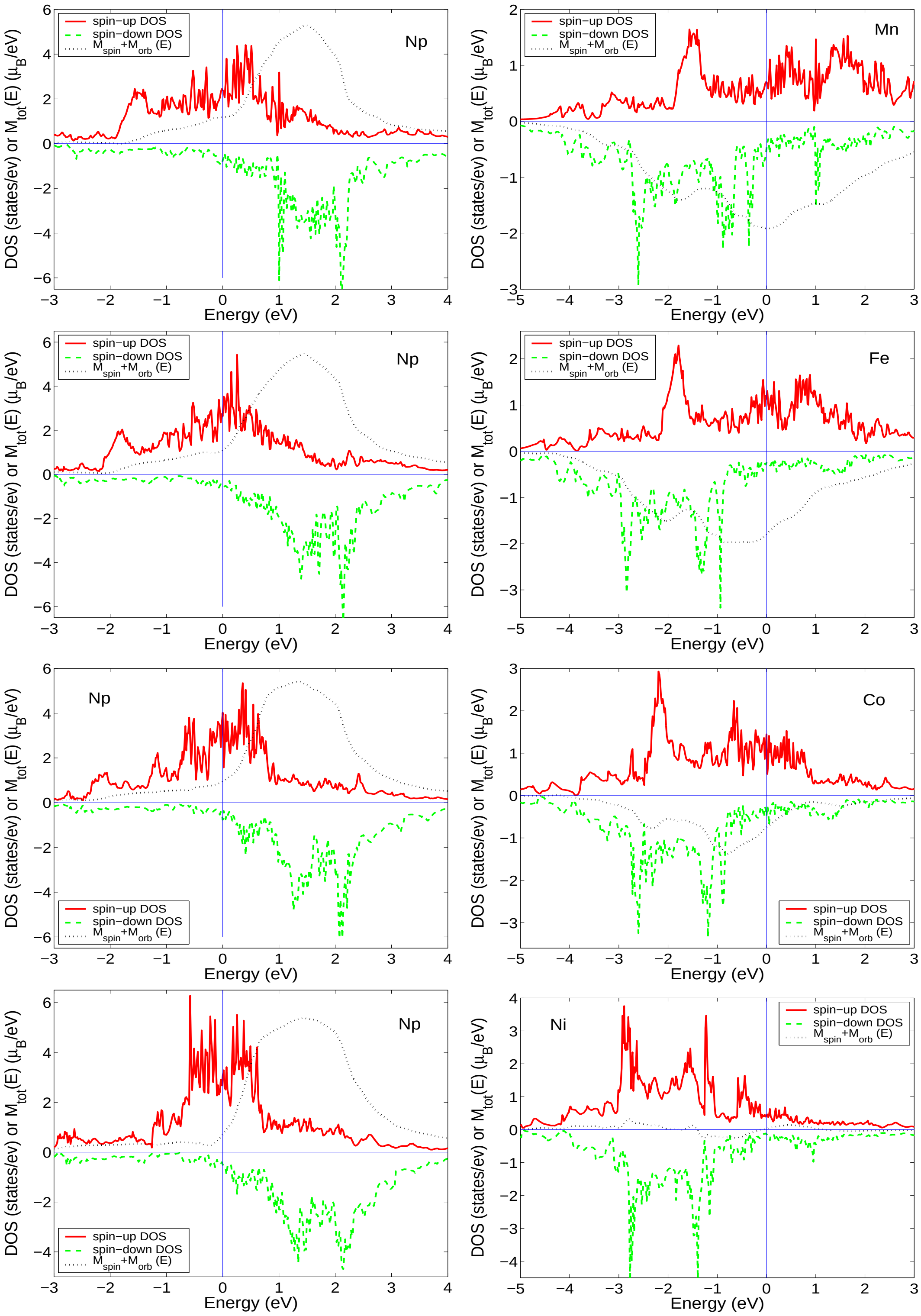

FIG. 4: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Np and M in the compounds NpM_2 ($M = Mn, Fe, Co, Ni$). Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

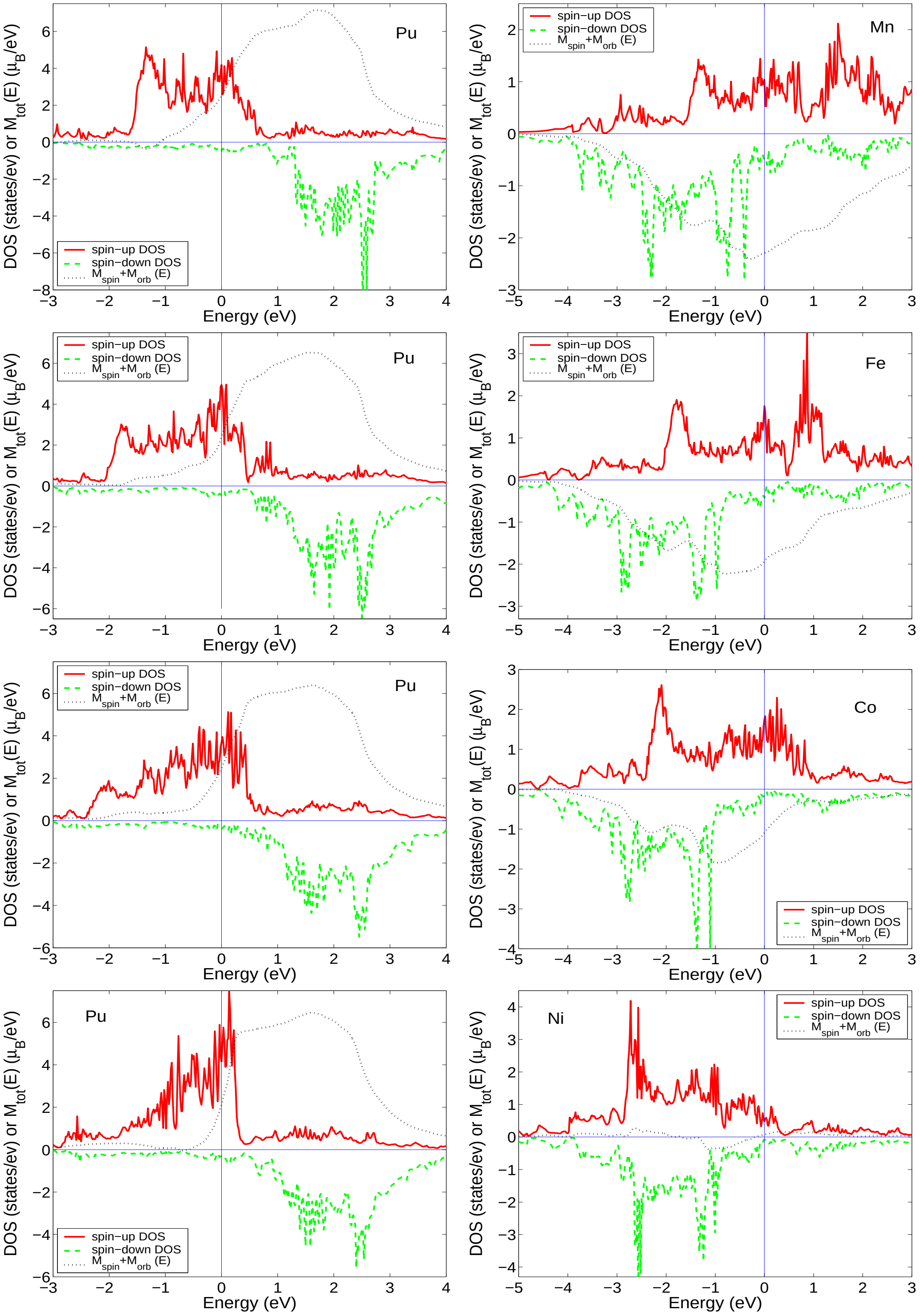

FIG. 5: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Pu and M in the compounds PuM_2 ($M = Mn, Fe, Co, Ni$). Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

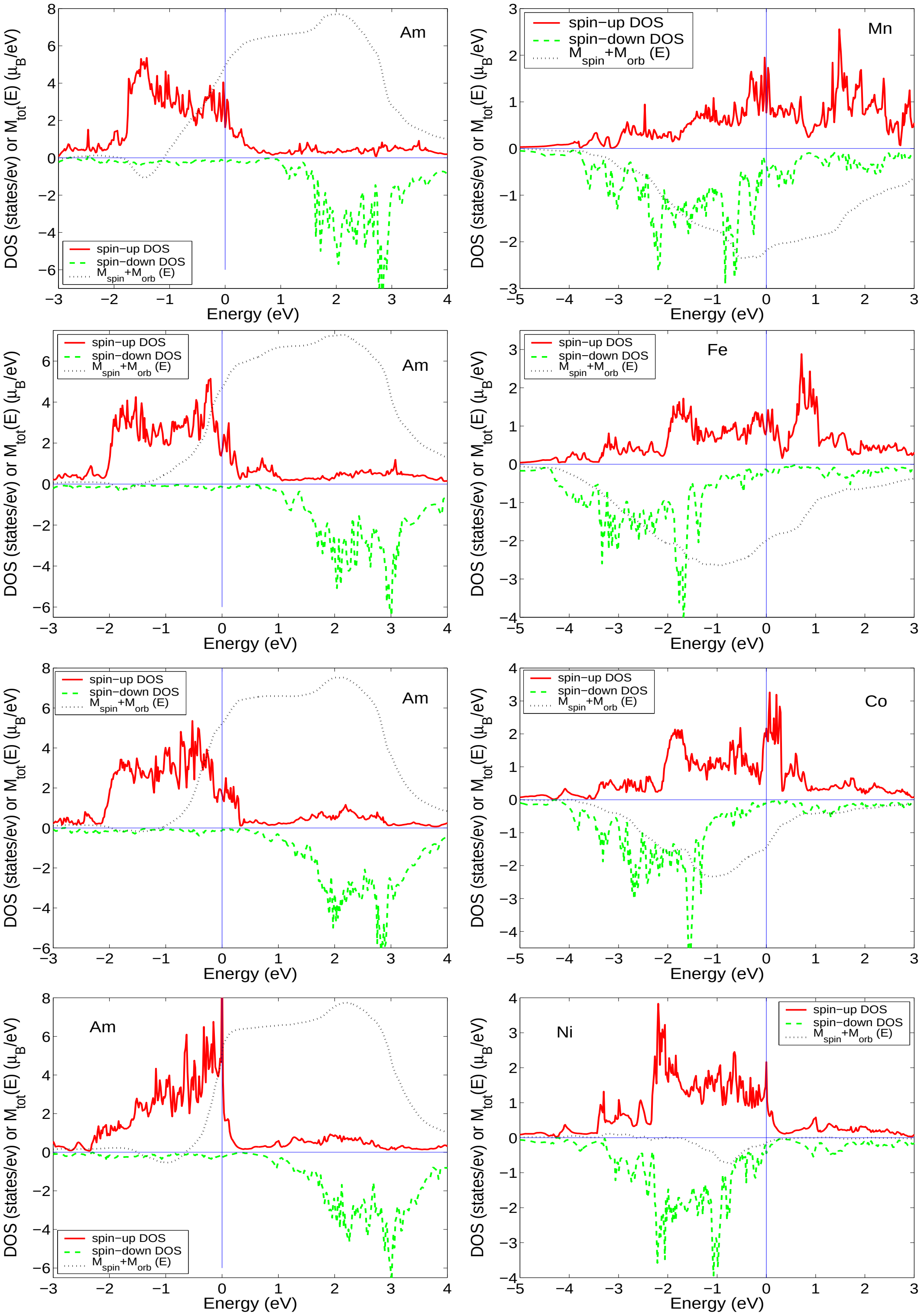

FIG. 6: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Am and M in the compounds AmM_2 ($M = Mn, Fe, Co, Ni$). Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

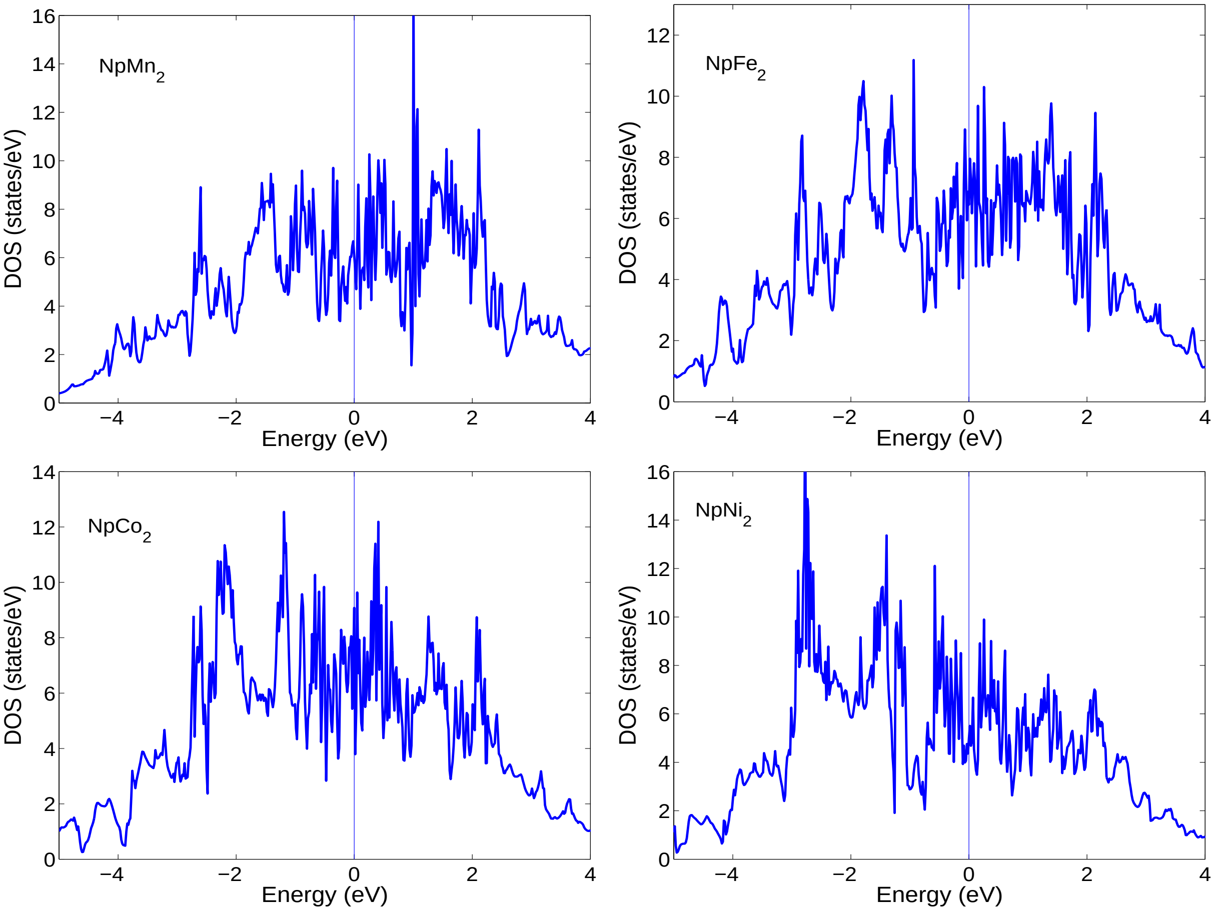

FIG. 7: Total densities of states for the compounds NpM_2 ($M = Mn, Fe, Co, Ni$) obtained from spin-polarized calculations. Fermi level is taken as zero energy.

should also mark that in the case of $PuCo_2$ the cancellation of big magnetic moments on the atoms takes place and, so, the remaining magnetization may be related with inaccuracy. In other plutonium's compounds (as well as in the case of pure Pu) the magnetic moments obtained should be thought as false moments. Further, going to the analysis of the moments on atoms, we can note practically full absence of magnetic moments on the atoms of nickel (in limits of accuracy), though metallic nickel has magnetic moment 0.56 μ_B. Also, orbital part of magnetization for the atoms of transition metals is always small, which is very similar to the situation with pure transition metals. It is interesting also the strong dependence of the orbital moment of neptunium atom on the transition metal which is coupled with it.

Going to the analysis of DOS, we can note, that in most cases the strong hybridization can be noticed between 5f-states of actinides and 3d-states of transition metals. It is interesting to note however, that as it follows from the calculations (see Fig. 4- 6), the hybridization

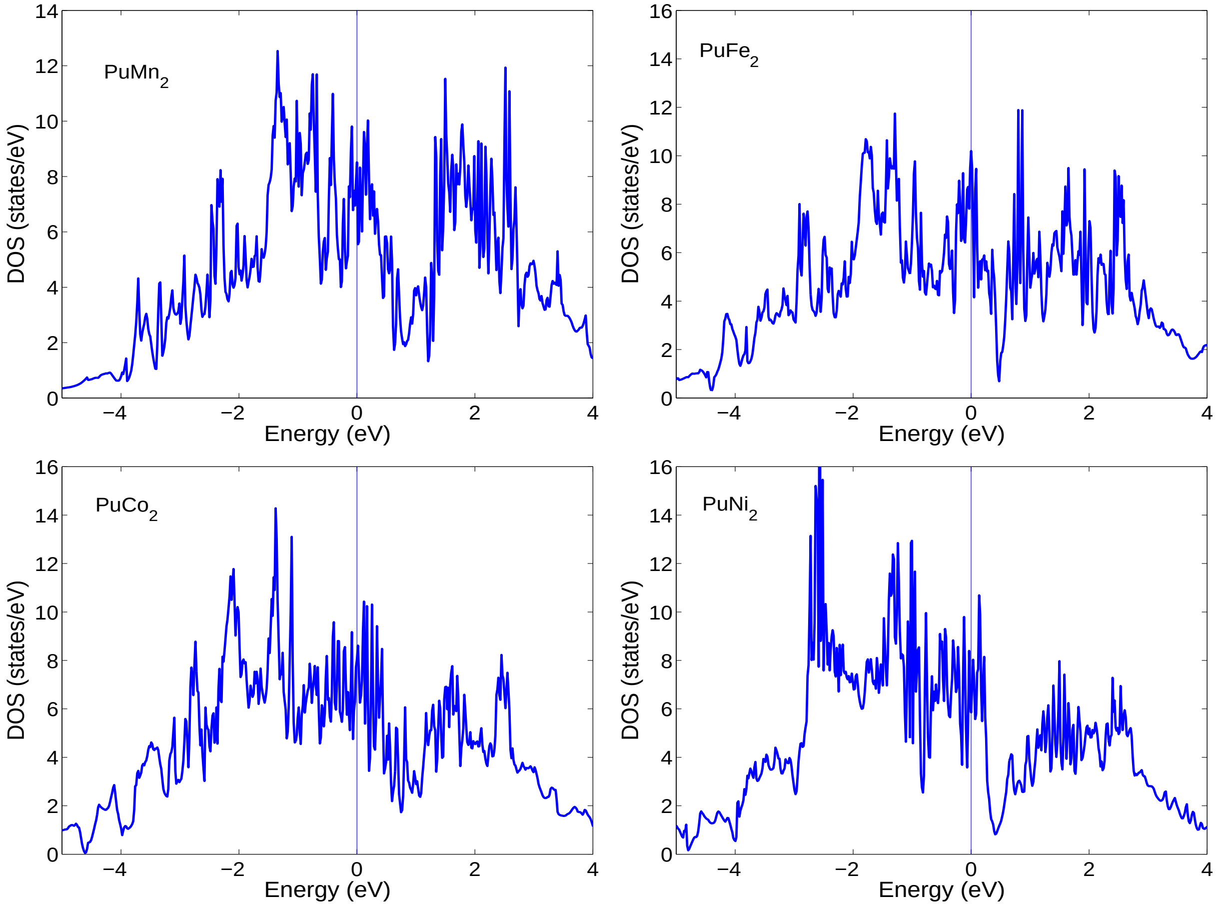

FIG. 8: Total densities of states for the compounds PuM_2 ($M = Mn, Fe, Co, Ni$) obtained from spin-polarized calculations. Fermi level is taken as zero energy.

in all cases is present only between the spin-up states, because the spin-down states of transition metal situate below Fermi level while the spin-down states of actinide lay higher than Fermi energy. There is some difference, however (see Fig. 1- 3), between DOS of the compounds of different actinides. We can see a gradual shift of 5f and 3d states relatively each other for Np compounds (3d-states of transition metal are going down). This shift is weaker in Pu compounds, and it is practically absent for Am compounds. The shift of 3d and 5f-states in the neptunium compounds might be a cause of a big difference in orbital moments of neptunium atoms in its compounds. Also, the absence of magnetism on nickel atoms can be explained by the fact, that in all cases 3d-states of nickel are almost completely under Fermi level. And while for the compounds of Np and Pu this fact is the consequence of above mentioned shift between 5f and 3d-states, for Am compounds this fact is the result of joint gradual lowering of 5f and 3d-states relatively Fermi level in such a manner, that

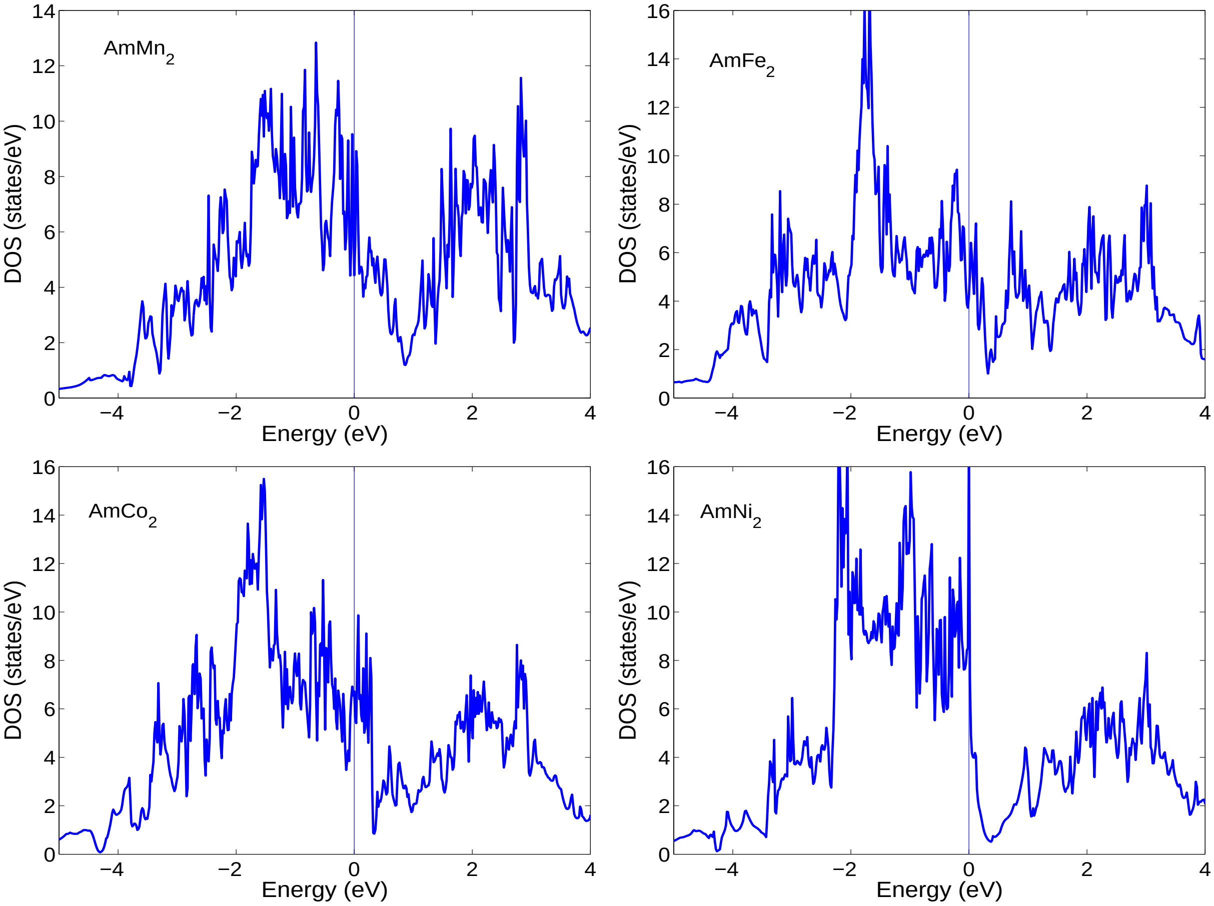

FIG. 9: Total densities of states for the compounds AmM_2 ($M = Mn, Fe, Co, Ni$) obtained from spin-polarized calculations. Fermi level is taken as zero energy.

3d-levels of transition metal again appear below Fermi energy in the case of $AmNi_2$.

Thus, the present consideration indeed confirms the assumption of the importance of hybridization in the compounds under studying for the formation of magnetic structure. This hybridization often allows the possibility of local magnetic moment formation despite the violation of Hill's rule.

IV. PuU: MAGNETIC STRUCTURE, TOTAL AND PARTIAL DOS. COMPARATIVE ANALYSIS OF THE COMPOUNDS OF PLUTONIUM $PuU, PuNp, PuAm$.

In the present work the studying of the compounds of plutonium and other actinides has been prolonged with the investigation on PuU. The corresponding results (together with results for PuNp and PuAm) are given in the Figures 10- 12 and in the Table III. As it was already stated in the previous reports, the formation energy for PuNp is positive, i.e. pure Pu and Np are more stable that their compound. On the contrary, the system Pu-Am appeared to be stable (i.e. this system has negative energy of formation) for all the percentages of Am in it. The calculation, which has been carried out in the present work, has resulted in the formation energy of PuU, equal to 0.182eV/atom, which means the instability of the compound. Thus, if we base on the calculations performed within density functional theory, then of three elements (U, Np, and Am) only Am is able to stabilize plutonium in its fcc structure.

Comparing the non-spin-polarized and spin-polarized calculations, it can be noticed, that however the general picture is changed with adding the spin-polarization, the main result is preserved unchanged. This result consists in the weak hybridization of 5f-electrons of plutonium and uranium in PuU, in increasing of the hybridization between 5f-electrons of actinides in PuNp and in very high degree of hybridization in the case of PuAm. It seems, that strong hybridization between 5f-electrons of plutonium and americium is the explanation for the negative formation energy and for the stability of the compound of plutonium and americium.

As it is seen from the Table III, the big magnetic moments are obtained in the calculations for all compounds. At the same time, we have no any experimental evidences about magnetism in these compounds. Some explanation of this contradiction can be found, however, in the DOS examining.

If we take a look of the Figures 10 and 11 (the calculation with spin-polarization included), we will be able to conclude, that in the compounds under studying the formation of the

TABLE III: Atomic magnetic moments (in Bohr's magnetons) of actinides in their compounds.

Compound	Atom	M_{spin}	M_{orb}	M_{total}
PuU	Pu	4.07	−1.68	2.39
	U	−0.87	0.42	−0.45
$PuNp$	Pu	3.95	−1.80	2.15
	Np	2.24	−1.60	0.64
$PuAm$	Pu	4.63	−2.20	2.42
	Am	5.92	−0.69	5.24

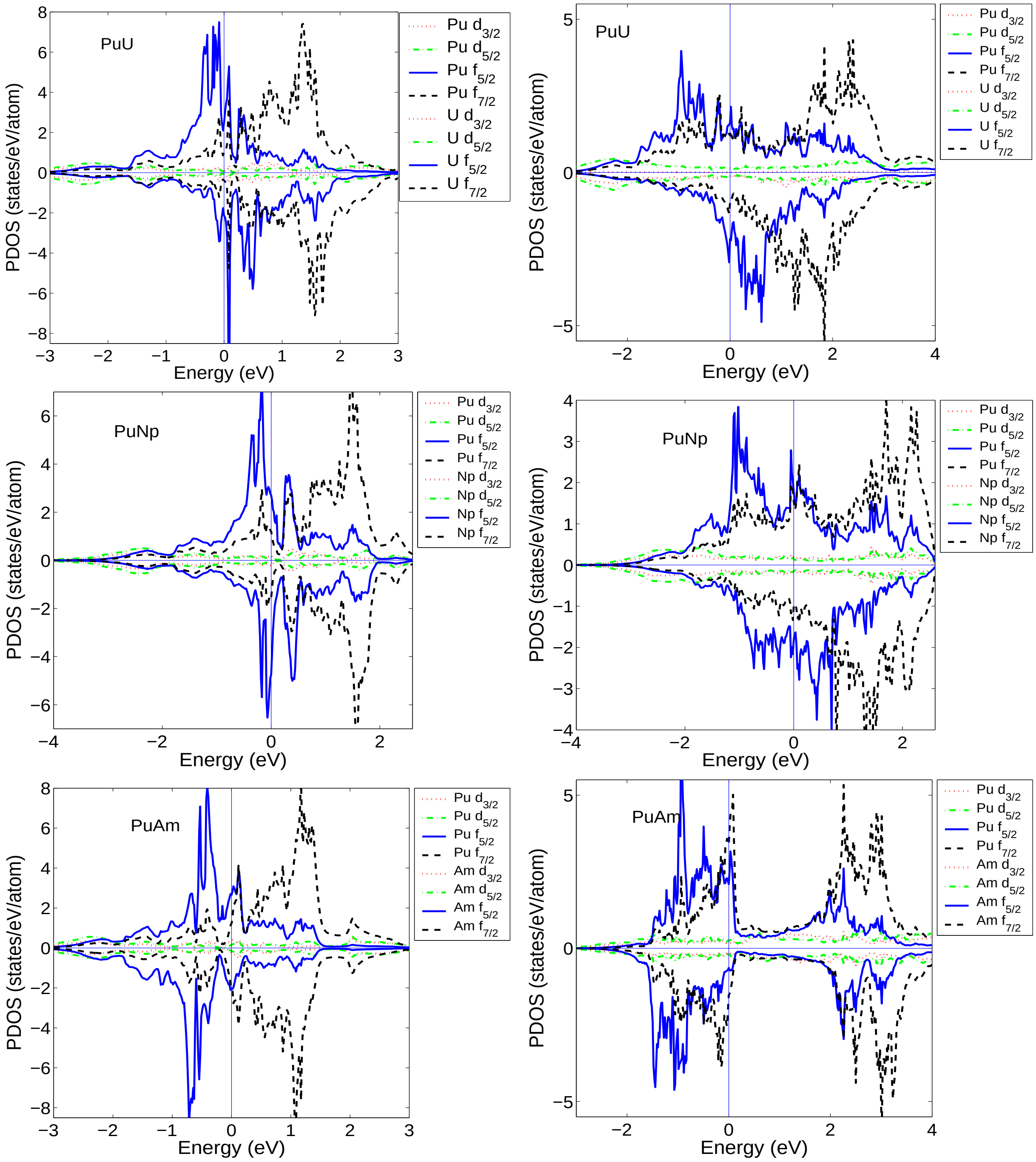

FIG. 10: Partial densities of states (PDOS, states/eV) from nonmagnetic (left panel) and magnetic (right panel) calculations of the compounds PuM ($M = U, Np, Am$). Fermi level is taken as zero energy. The states of M are given with negative sign for the sake of convenience.

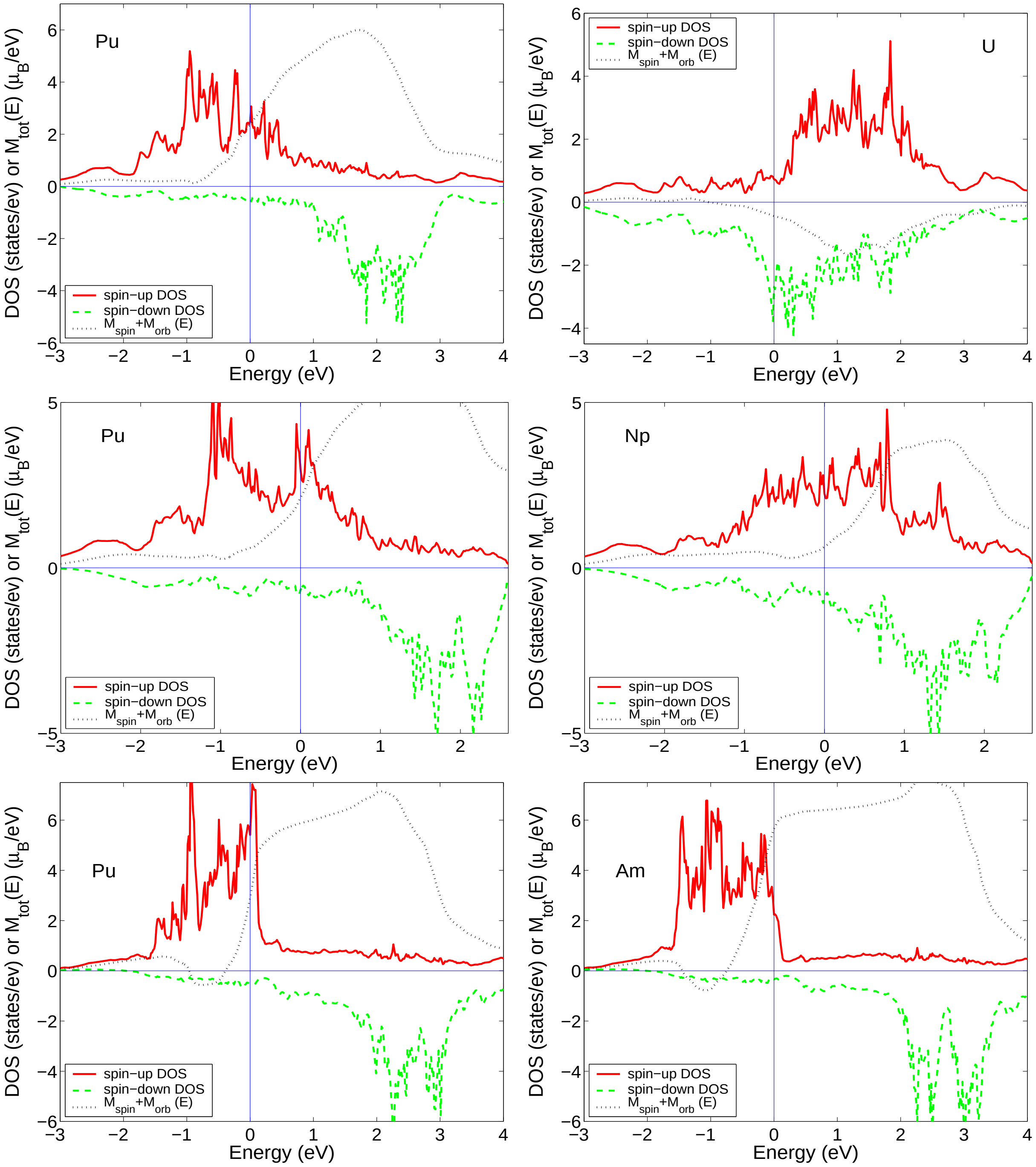

FIG. 11: Spin-resolved DOS and magnetic moment function (see Chapter III) for Pu and M atoms in the compounds PuM $(M = U, Np, Am)$. Fermi level is taken as zero energy.

electronic structure on atoms U and Np is a result of exchange and spin-orbit splitting of bands, and moreover the spin-orbit prevails. Further, in Am the exchange splitting is dominated, while in Pu both effects have almost equal importance. Thus, both the spin-orbit and the exchange splitting of bands are very important when we are studying these

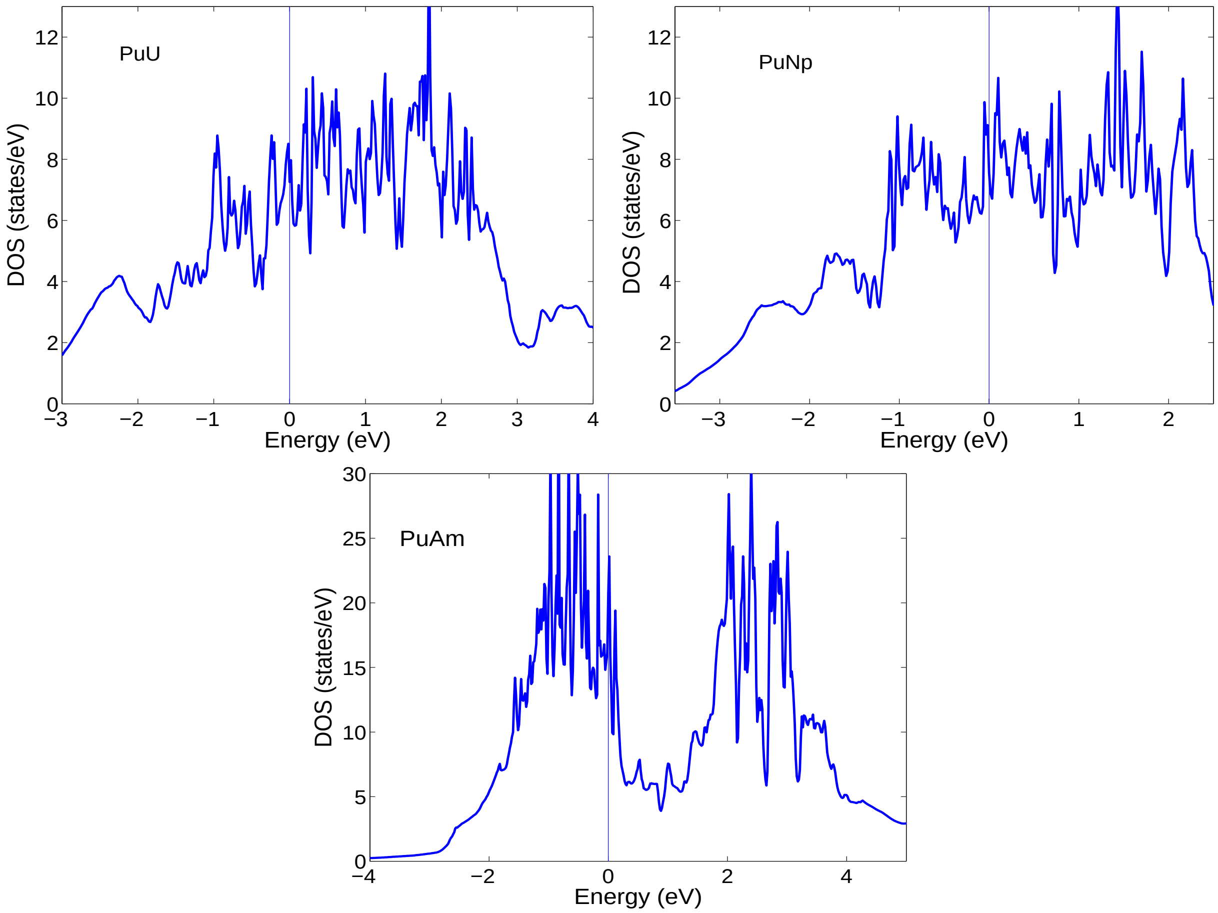

FIG. 12: Total densities of states (DOS, states/eV) from magnetic calculations of the compounds PuM ($M = U, Np, Am$). Fermi level is taken as zero energy.

plutonium compounds. In relation to this it is necessary to point out, that while in the spin-orbit interaction calculation we don't make any simplifying assumptions (i.e. we can say, that this term of Hamiltonian is treated with high accuracy), in the calculation of exchange there is a several simplification of general acceptance. This simplification consists in the substitution the corresponding two-particle operator (nonlocal) with one-particle (local) operator. Thus, in the circumstances, when there is a thin balance between above two interactions, the inaccuracies involved in the calculation of exchange might lead to the quite inadequate results. One of the ways of clearing the situation with plutonium compounds (and with pure Pu too), in which the above balance is always present in some degree, might consist in the working out the relativistic Harthree-Fock theory and corresponding computer code. As it is known in Harthree-Fock theory the exchange is treated without any simplifications, and, so this approach might be useful. Our nearest plans include the work in this direction.

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[1] H. H. Hill, in: Plutonium 1970 and Other Actinides/Ed. W. N. Miner, New York: Metallurg. Soc. AIME, 1970.

[2] V. Sechovsky and G. Hilscher, Physica Ser. B **130**, 207 (1985).

[3] J. Perdew, S. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[4] A. L. Kutepov and S. G. Kutepova, J. Phys.: Condens. Matter **15**, 1 (2003).

[5] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).