UCRL-TR-216116

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Comparative Analysis of Monochalcogenides of Actinides

A. L. Kutepov

October 12, 2005

Disclaimer

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

Delivery 4. Tasks 4.1-4.3

COMPARATIVE ANALYSIS OF MONOCHALCOGENIDES OF ACTINIDES

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

The series of monochalcogenides of actinides NpM, PuM, and AmM ($M = S, Se, Te$) has been studied with relativistic spin-polarized density functional theory. The electronic and magnetic structure of the compounds has been investigated. It has been shown that the hybridization between 5f-electrons of actinides and p-electrons of S, Se, or Te is practically absent. But there is a transfer of electrons from one element to another. This transfer, apparently, is a cause of a crystal field splitting of the bands, which is superimposed on the spin-orbit splitting. The experimental magnetic properties of the above compounds may be explained in this simple picture, obtained from non-spin-polarized calculations. Accounting for magnetism leads to the excessive spin splitting of the bands and to the disagreement with experimental data. So, present work can be considered as one more evidence, that it is necessary to develop more elaborated theory than DFT for study of magnetism in actinides and their compounds.

I. INTRODUCTION

Although the light actinides are well described within density functional theory (DFT), the local density approximation (LDA) fails in general to describe elemental Pu at high temperature and the actinides past plutonium. The using of relativistic spin-polarized DFT (RSP-DFT) allows us to improve the ground state properties description but fails in describing of the magnetic properties. In particular, false magnetic moments are obtained in this theory for Pu. In previous reports it has been shown that the same problem takes place in the compounds of actinides A_3M (M= Al, Ga, In) and AM_2 (M= Mn, Fe, Co, Ni). The reason may be that in this spin-polarized relativistic density functional theory the Kohn-Sham equation consists of the one-electron Dirac equation containing an effective scalar potential and an additional effective magnetic field that is the functional derivative of the exchange-correlation energy with respect to the spin magnetic moment only. This is an approximation in which orbital contributions to the magnetic moment are neglected. Since a complete methodology is currently unavailable, it may be instructive to have more results, obtained with the today's DFT-theory, to see better the defects in this theory and possible ways to improve the methodology. Therefore, the present work was aimed to study of one more type of actinide's compounds AM (A= Np, Pu, Am; M= S, Se, Te). The purpose of the investigation was to check whether the theory fails again in describing of the magnetic properties, and, on the other hand, to follow the changing of the electronic structure of the compounds when we pass from one actinide to another and to study the role of accounting for magnetism in the electronic structure formation (from the point of view RSP-DFT).

The report is organized as follows. In the chapter II the calculational method and parameters used are described. The results obtained for the compounds NpM, PuM, and Am $(M = S, Se, Te)$ are discussed in the chapter III. Lastly, in section IV the conclusions and future plans are offered.

II. THE METHOD AND PARAMETERS

Density functional theory in generalized gradient approximation, [1], 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

TABLE I: Calculated equilibrium distances between atoms of actinide (Å) for the compounds AM ($A = Np, Pu, Am$, $M = S, Se, Te$). The results from non-spin-polarized calculations are shown in the brackets.

	S	Se	Te
Np	3.91(3.81)	4.06(3.99)	4.31(4.25)
Pu	3.94(3.83)	4.08(3.99)	4.36(4.28)
Am	4.03(3.91)	4.19(4.07)	4.41(4.32)

formulas of this method had been given earlier, [2].

All studies for the compounds AM ($A = Np, Pu, Am$; $M = S, Se, Te$) have been performed with the experimental cubic crystal structure of $NaCl$ type. 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.

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 for total energy convergence which should be better than 1 mRy per atom.

The integration over Brillouin zone was carried out with improved tetrahedron method, [3]. 102 irreducible **k**-points were used in all calculations presented.

III. THE RESULTS OF STUDYING OF THE COMPOUNDS AM ($A = Np, Pu, Am$; $M = S, Se, Te$).

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

TABLE II: Atomic magnetic moments (Bohr's magnetons) of actinides in the compounds of neptunium, plutonium, and americium in comparison with the existing experimental data, [4–6].

Compound	M_{spin}	M_{orb}	M_{total}	M_{exp}
NpS	2.98	-2.70	0.18	0.9;1.49
$NpSe$	3.20	-2.89	0.31	?
$NpTe$	3.73	-3.32	0.41	?
PuS	4.87	-2.09	2.78	0
$PuSe$	4.99	-2.14	2.85	0
$PuTe$	5.13	-2.23	2.90	0
AmS	6.14	-0.44	5.70	?
$AmSe$	6.23	-0.40	5.83	?
$AmTe$	6.33	-0.35	5.98	?

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.

As it is seen from the Table I, the calculated distances between the atoms of actinides (and, therefore, equilibrium volumes) are bigger than the corresponding distances in the compounds AM_2 (M= Mn, Fe, Co, Ni) and A_3M (M= Al, Ga, In) (see previous reports). They are also much bigger than the Hill's constants, [7], for Np ($d_H \approx 3.2\mathring{A}$) and Pu ($d_H \approx 3.4\mathring{A}$). So, in agreement with the Hill's condition, we can expect of some magnetic structure in these compounds of actinides. However, it seems (see Table II), that only compounds of neptunium have magnetic moments (for americium monochalcogenides the experimental information is absent). Plutonium's compounds are found to be paramagnetic in experiments at low temperatures. The theoretical results are completely different. We have small magnetic moments on neptunium atoms (due to the cancellation of spin and orbital moments) and, on the other hand, big moments on plutonium atoms. Therefore, the situation is not very distinctive from the pure Pu: again we have big and false magnetic moments on the atoms.

Looking for the reason of such defect of the theory, it is useful to analyze the partial densities of states (PDOS, Fig. 1-3). It seems, that non-spin-polarized calculations (NSP, left

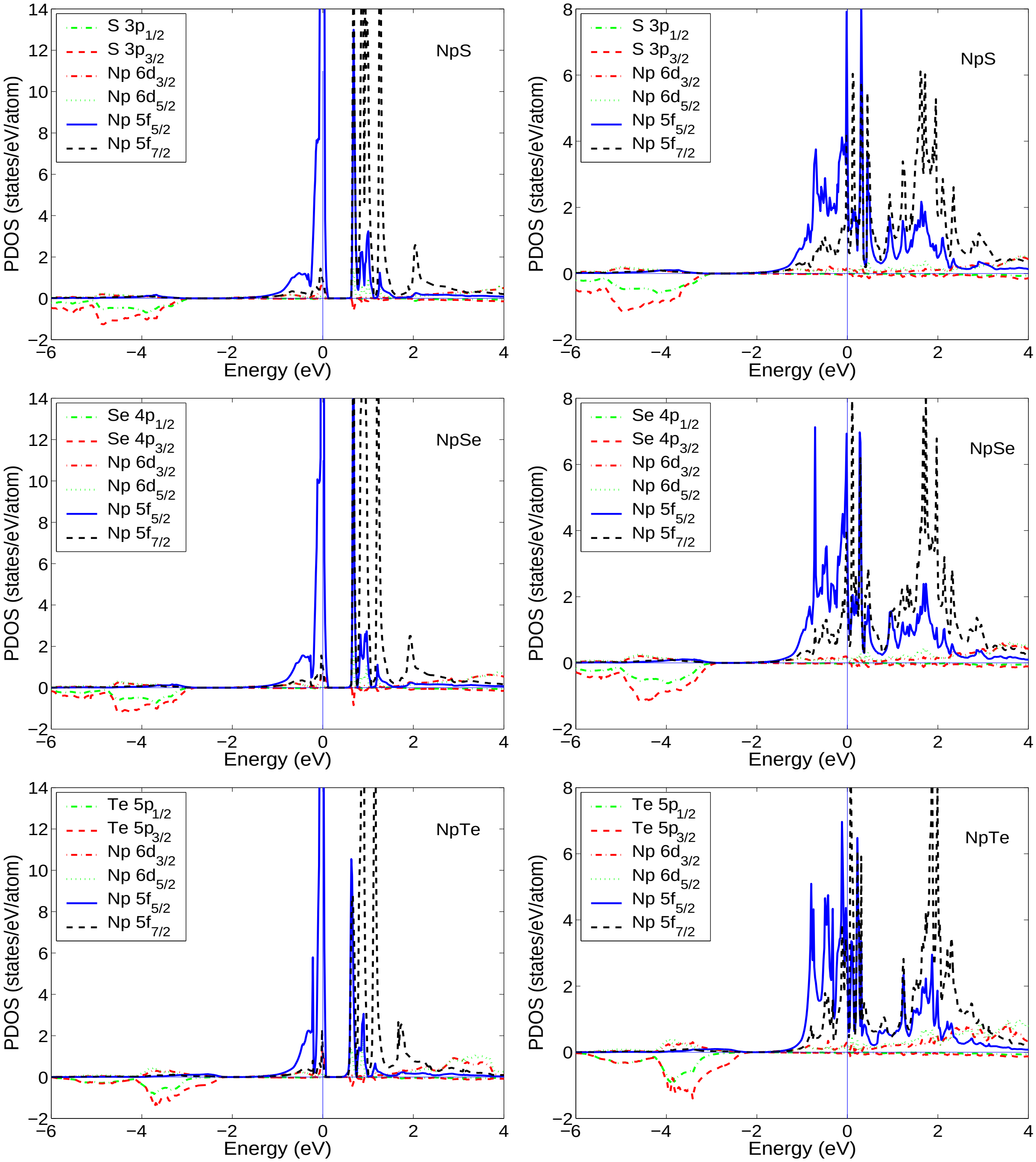

FIG. 1: Partial densities of states for the compounds of neptunium from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy. The DOS for S, Se, and Te are given with negative sign for the convenience of viewing.

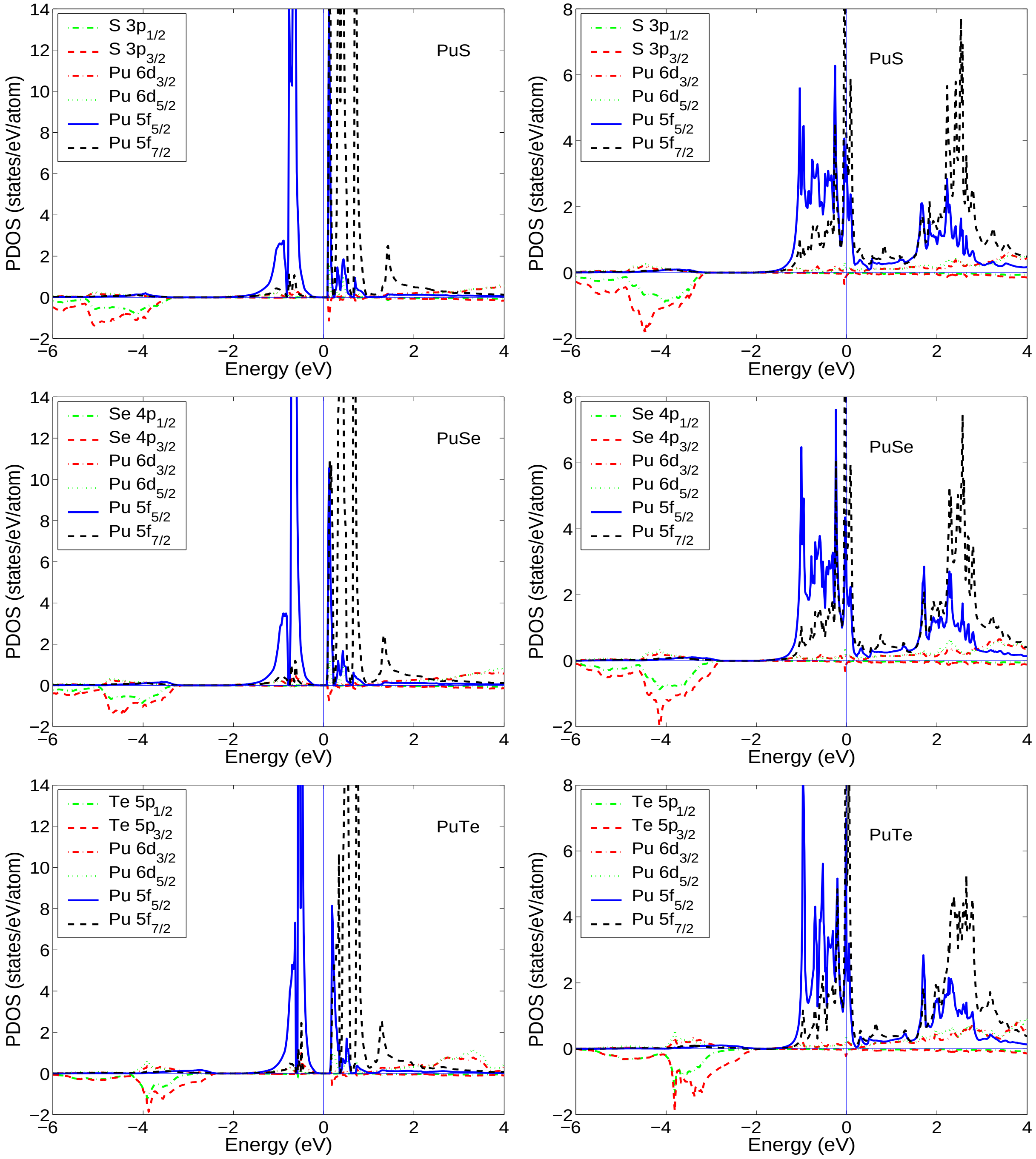

FIG. 2: Partial densities of states for the compounds of plutonium from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy. The DOS for S, Se, and Te are given with negative sign for the convenience of viewing.

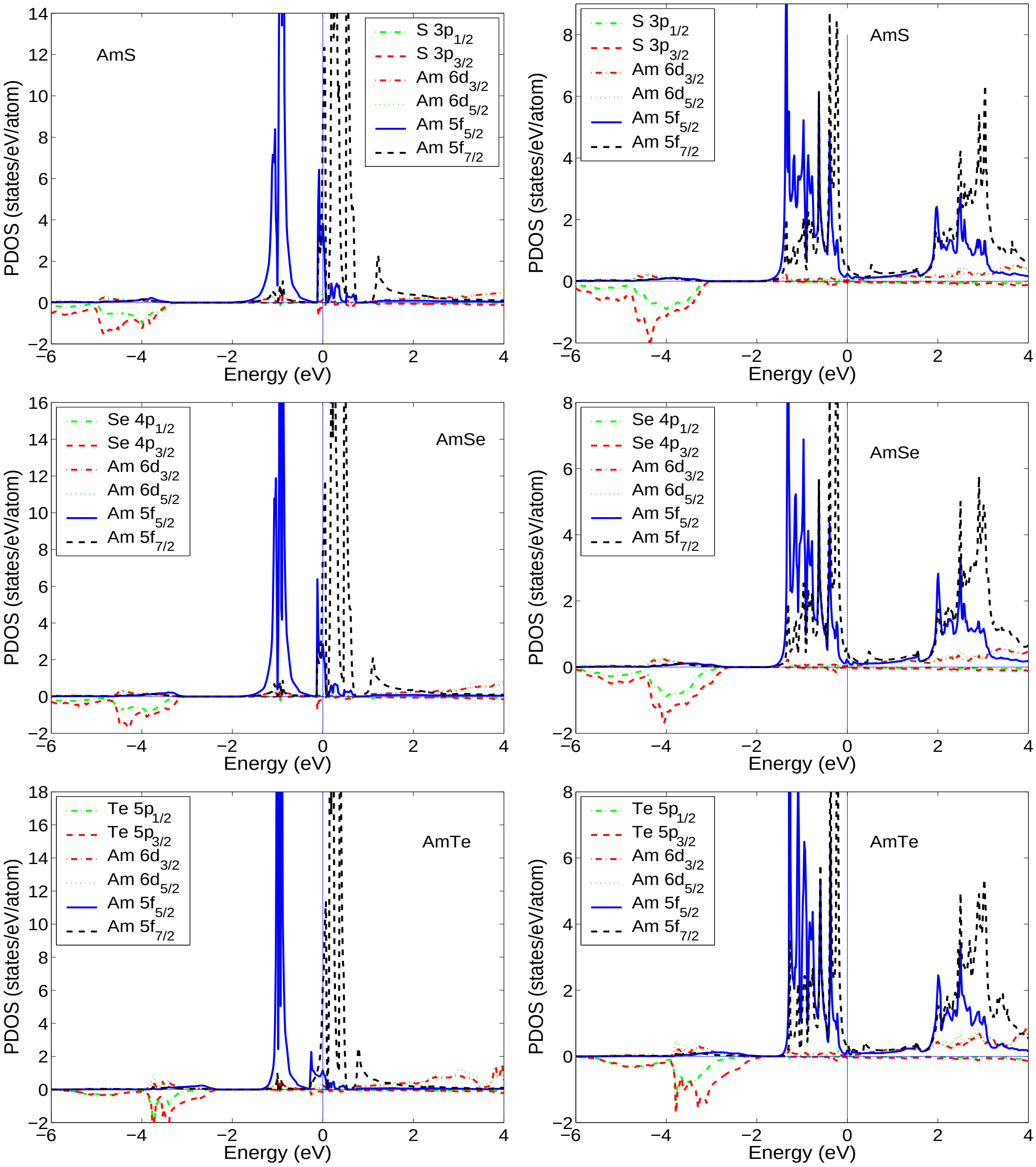

FIG. 3: Partial densities of states for the compounds of americium from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy. The DOS for S, Se, and Te are given with negative sign for the convenience of viewing.

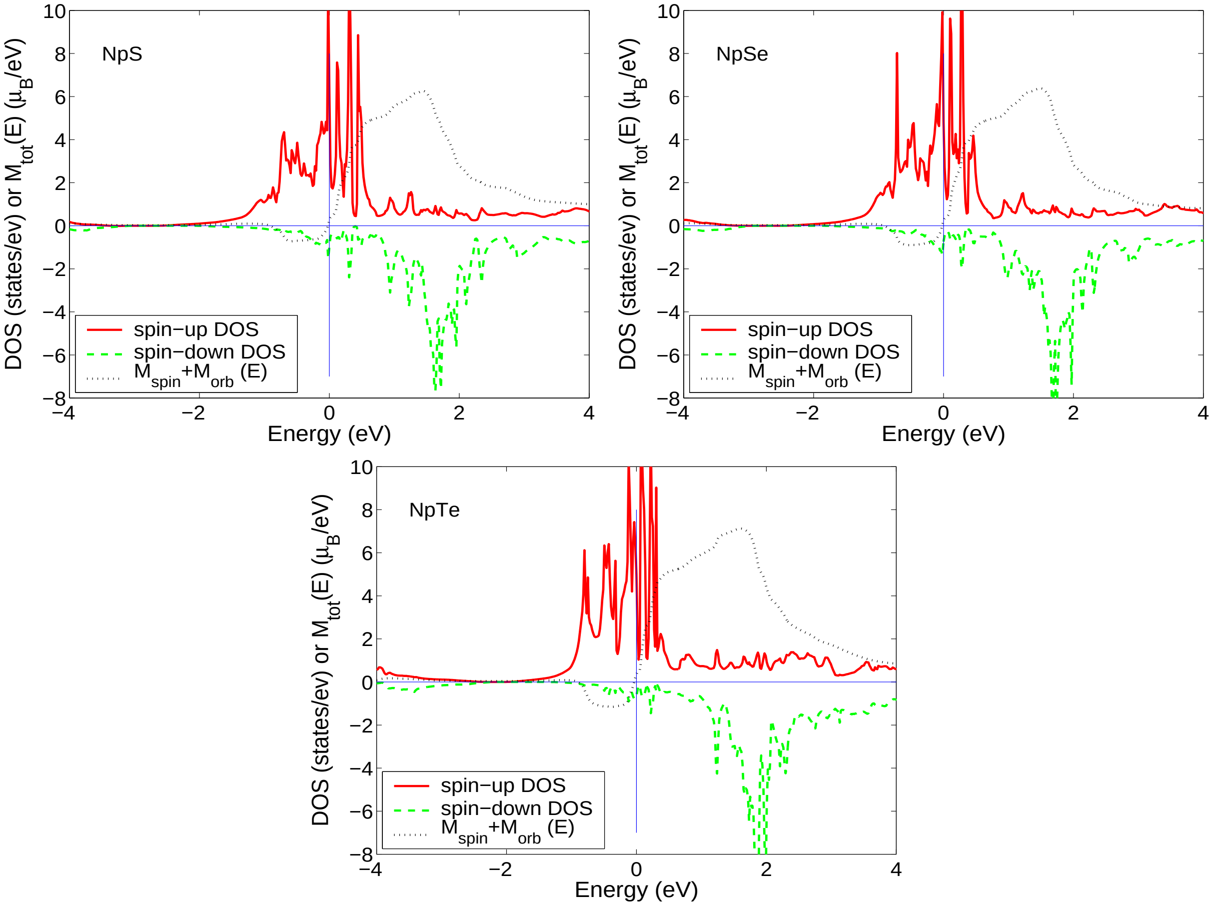

FIG. 4: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Np in the compounds NpM $(M = S, Se, Te)$. Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

column in the Figures) give us more information, than spin-polarized calculations. It follows from NSP calculations, that spin-orbit splitting is mixed, obviously, with the crystal field splitting. This fact is seen from an occurrence of an additional $5f_{5/2}$ peak near the bottom of $5f_{7/2}$ bands and of an additional $5f_{7/2}$ peak in the interval 1-2 Ev above E_f. Further, in neptunium monochalcogenides Fermi level passes through the lower peak of $5f_{5/2}$ DOS, in plutonium compounds DOS at E_f is practically zero, and in americium monochalcogenides Fermi level passes through the peak $5f_{7/2}$ DOS. Thus, if we base on the non-spin-polarized calculations, then, apparently, it is possible for us to explain the occurrence of some magnetic moments on neptunium atoms (if we suppose that accounting for exchange splitting only a little polarizes partially filled $5f_{5/2}$ bands) and the absence of the moments on plutonium atoms (if we suppose that the part of $5f_{5/2}$ states splitted in the crystal field is completely

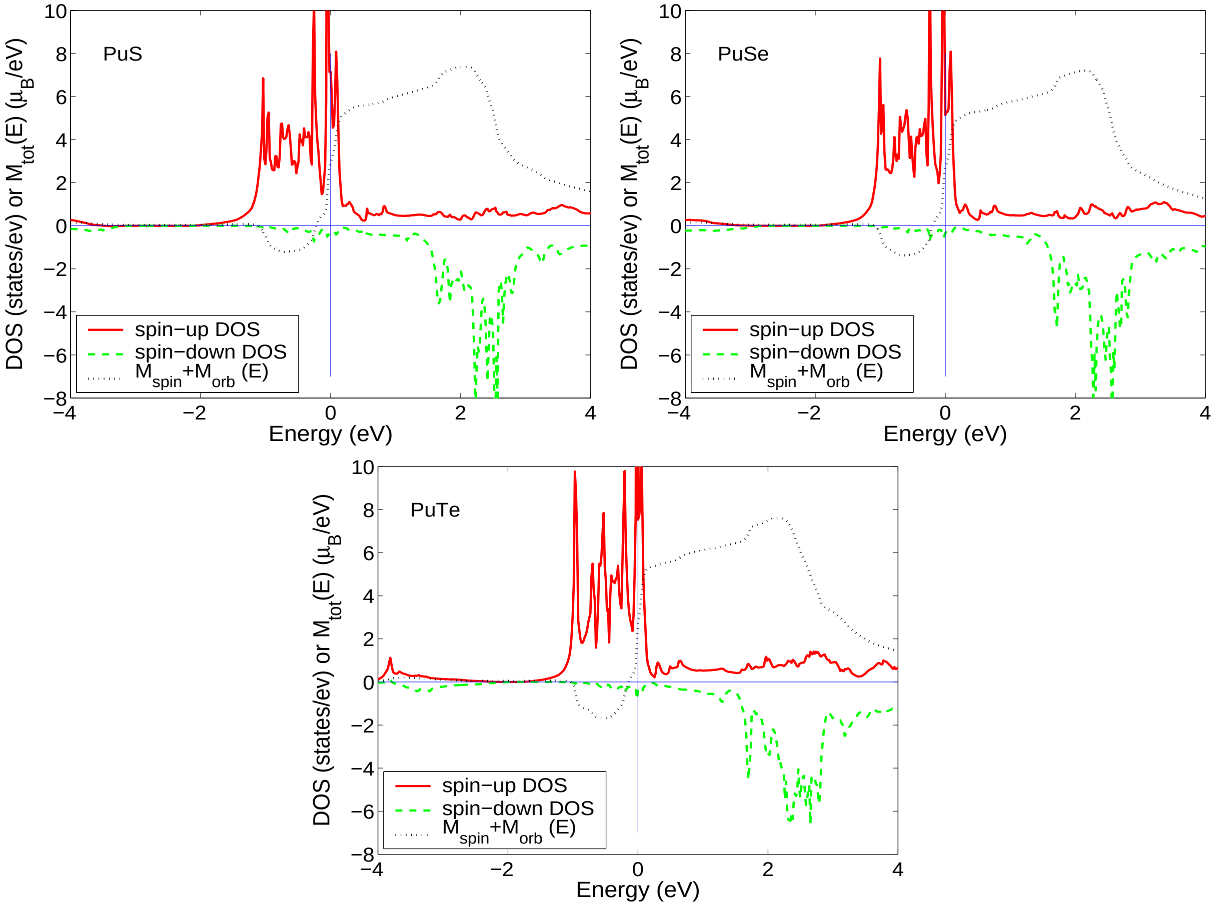

FIG. 5: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Pu in the compounds PuM ($M = S, Se, Te$). Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

filled with even number of electrons). In this picture there must be, obviously, some magnetic moments on americium atoms (due to partial filling of $5f_{7/2}$ states) and it is a pity, that we have no experimental data on americium monochalcogenides.

It is evident (from NSP calculations, as well as from SP calculations), that there is no any hybridization between electron states on atoms S, Se, or Te and on atoms of actinides. But there is some charge transfer and as a consequence of this transfer, there is an additional splitting (to the original spin-orbit in pure actinides) of electronic states in the electrostatic crystal field, as it was stated above.

As for the spin-polarized calculations, an excessive spin-splitting completely changes the scene depicted above and induces big spin magnetic moments in all the cases. This may be seen from the fact, that two big peaks of DOS (see Fig. 1-3 or 7-9) correspond to the electrons

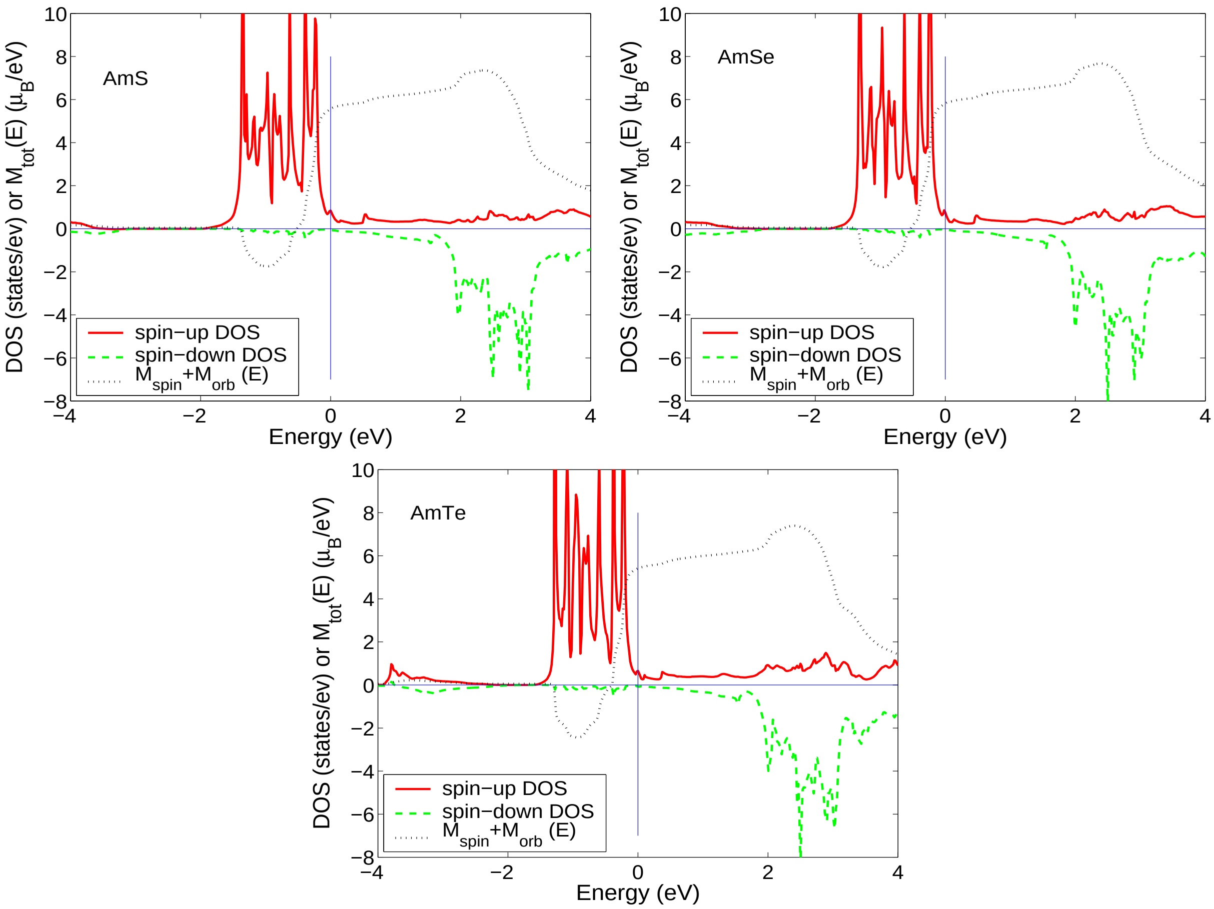

FIG. 6: Spin-resolved DOS and magnetic moment function (see text for explanation) for atoms Am in the compounds AmM ($M = S, Se, Te$). Fermi level is at zero energy. DOS for the states with spin (-1/2) is shown with negative sign.

of spin-up and spin-down, as it is evident from the Fig. 4-6. In the case of Np, these spin moments, indeed, are almost cancelled by orbital contribution (again in contradiction with experiments). Spin-orbit and crystal field splitting, obviously, are present in spin-polarized picture too, but in this case they look like small perturbations to the spin separated peaks of DOS.

IV. CONCLUSIONS AND PLANS FOR THE FUTURE

The investigation performed in this work on the monochalcogenides AM (A= Np, Pu, Am; M= S, Se, Te) has given us one more evidence of inadequacy of spin-polarized DFT when applied to the compounds of actinides. The pure effect of inclusion of magnetism into

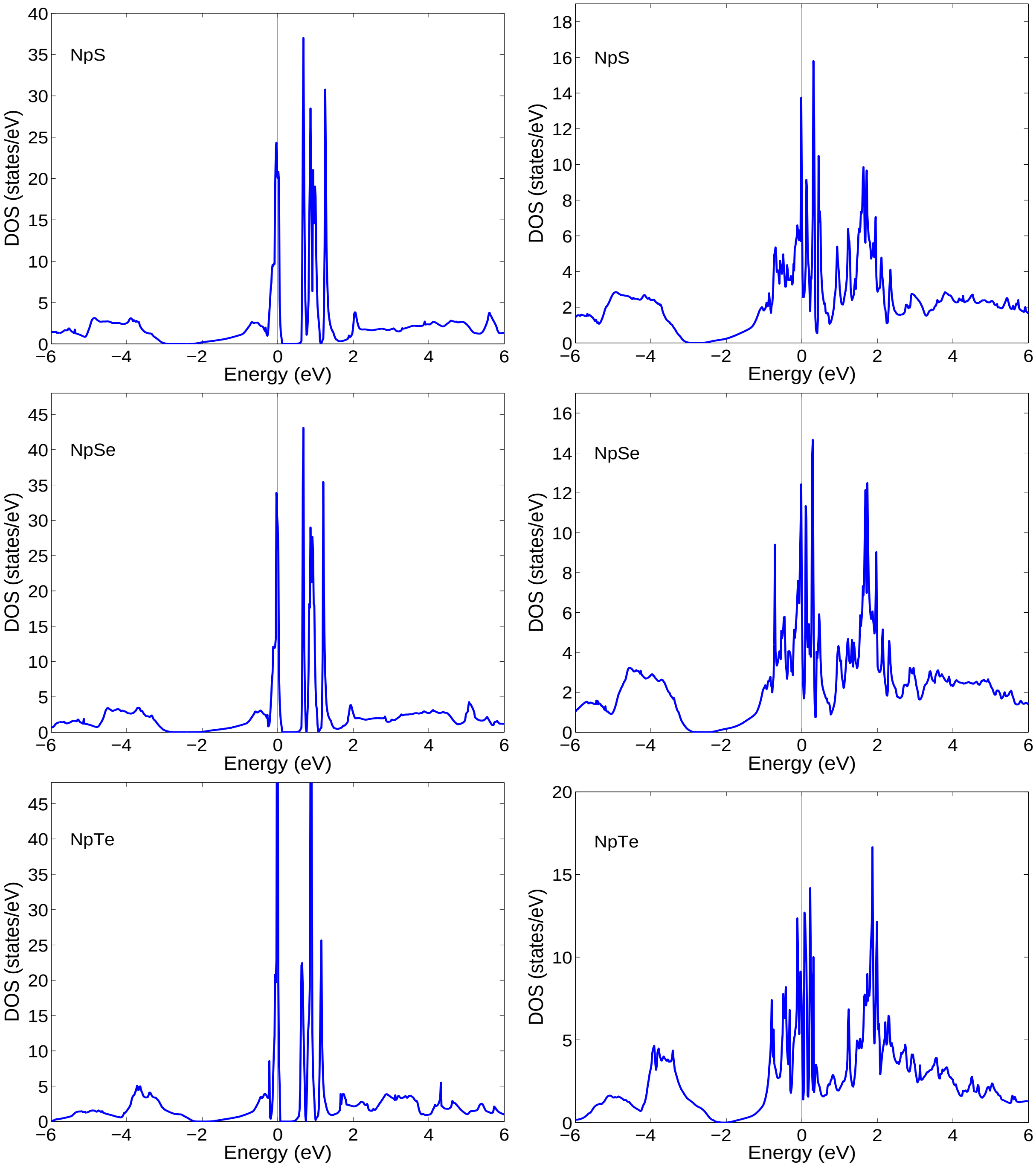

FIG. 7: Total densities of states for the compounds NpM ($M = S, Se, Te$) obtained from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy.

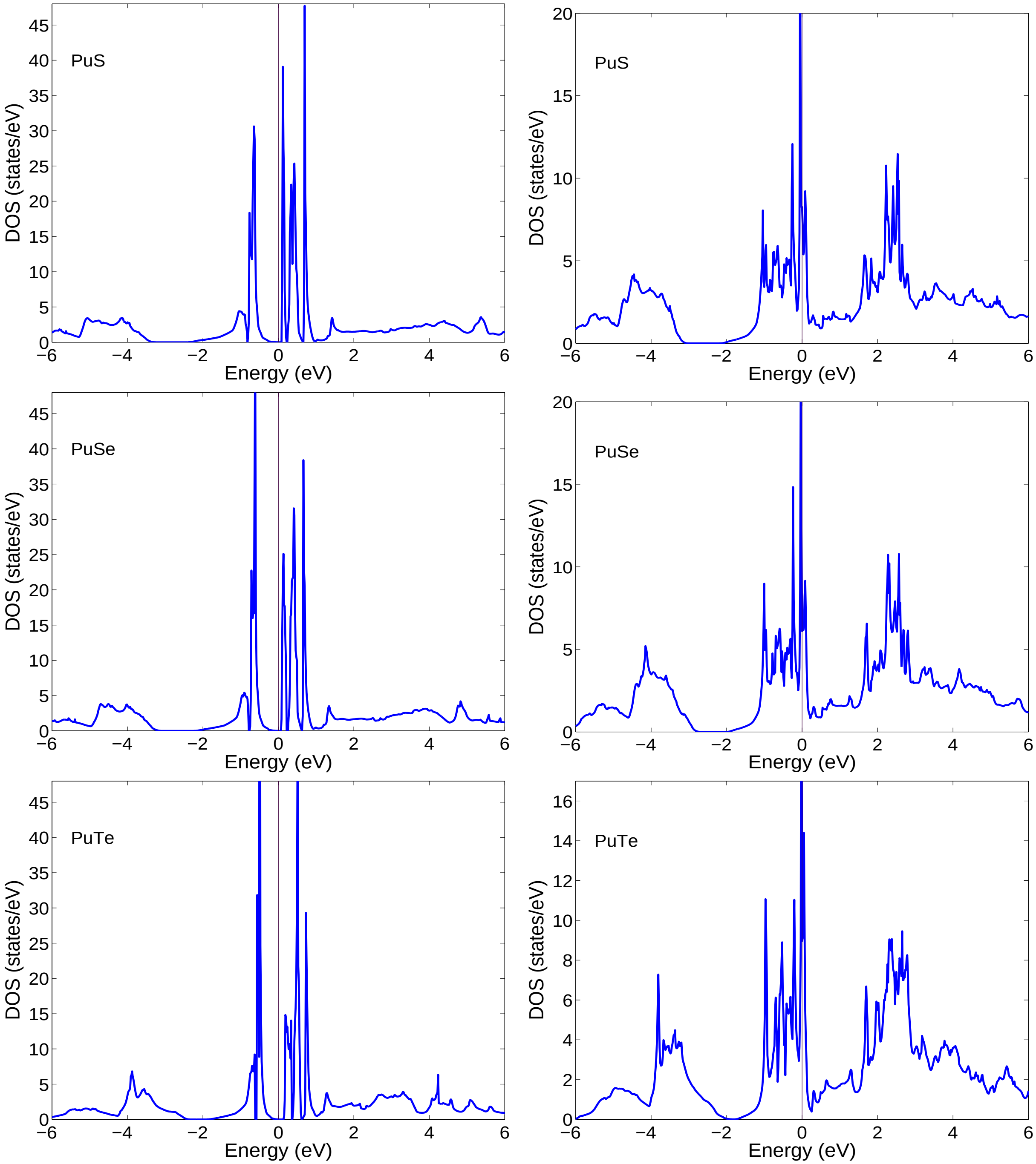

FIG. 8: Total densities of states for the compounds PuM ($M = S, Se, Te$) obtained from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy.

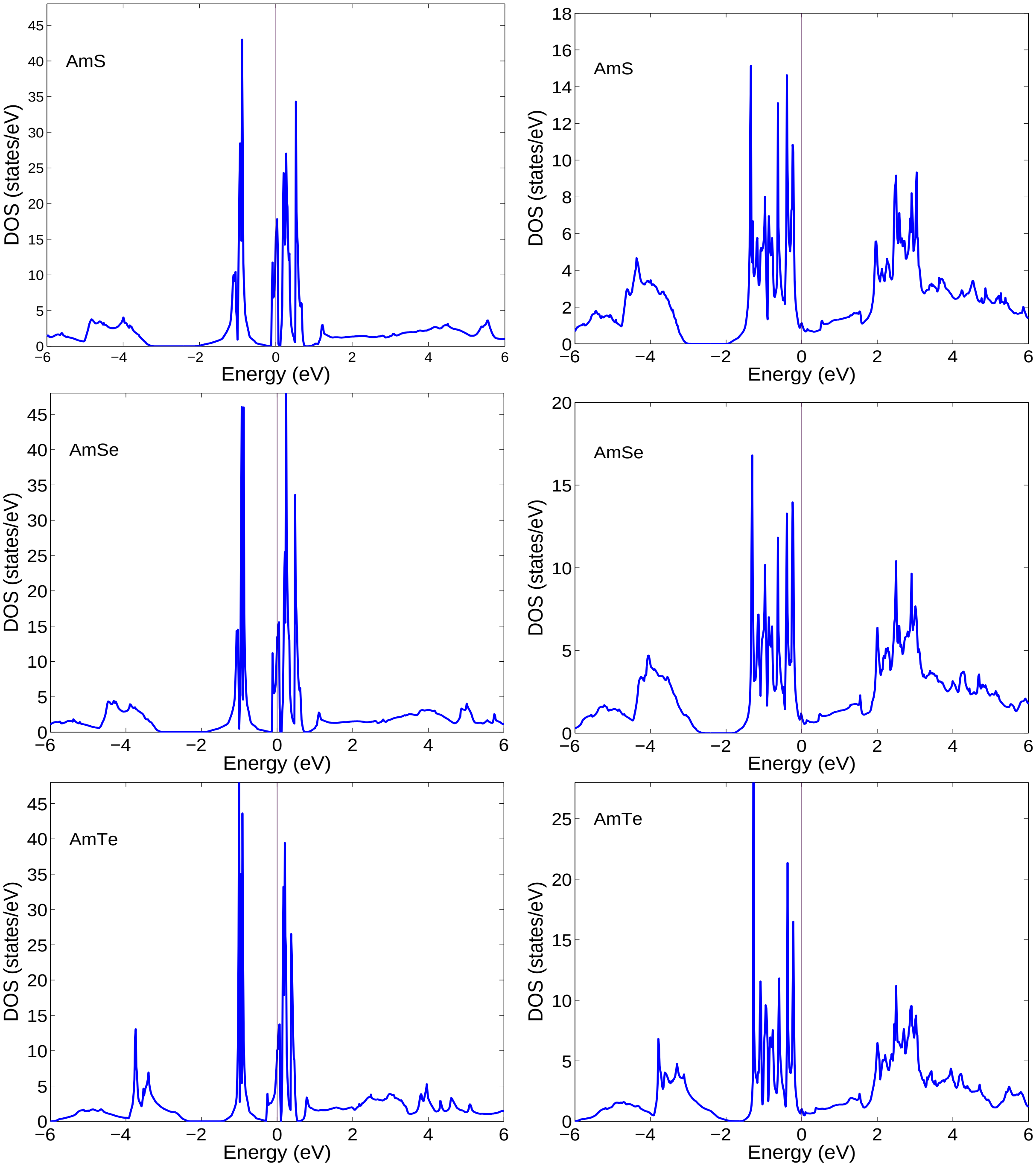

FIG. 9: Total densities of states for the compounds AmM ($M = S, Se, Te$) obtained from non-spin-polarized (left column) and spin-polarized (right column) calculations. Fermi level is taken as zero energy.

calculations is seen as if the spin splitting of bands was too strong. But the real cause of this defect is not so clear. It may be, as it has already been said in the Introduction, the absence of orbital polarization term in self-consistent equations of the theory. It is need to be said also, that spin (exchange) splitting itself is treated within DFT in a very approximate way, which may be fatal when applied to the actinides. Further, as it was proposed by Jim Tobin, in the situation with delicate balance between spin-orbit and exchange splitting, the relativistic effects of higher order (such as magnetic dipole) may play key role. Lastly, the reason may be in multielectron correlation effects, which are very difficult to describe in the theory.

So, our future plans are related with the developing of a relativistic Dirac-Hartree-Fock approach for the solids, as it was said earlier, to shed some additional light on the problem. This method treat accurately exchange and orbital degrees of freedom. We also plan to include the relativistic effects of higher order and hope to answer at least some of the existing questions.

---

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

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

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

[4] Troc R., Suski W., Fizyka i chemia ciala stalego., Ed. B. Stalinski, Wroclaw: Ossolineum, 1977. P.41.

[5] J. Rossat-Mignod, P. Burlet, S. Quezel, J. M. Effantin, O. Vogt, and H. Bartolin, Ann. de Chim. **7**, 471 (1982).

[6] Handbook of the Physics and Chemistry of the Actinides., V. 1,2, Eds. A. J. Freeman and G. H. Lander., Amsterdam: North-Holland, 1984-1985.

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