

## Electronic and magnetic properties of U-(Mo, W, V)-(Si, Ge) compounds crystallizing with U<sub>2</sub>Mo<sub>3</sub>Si<sub>4</sub>-type structure

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Compounds in the U-(Mo, W, V)-(Si, Ge) systems crystallize in the monoclinic U<sub>2</sub>Mo<sub>3</sub>Si<sub>4</sub>-type structure with interatomic distances between uranium atoms below and around the Hill limit. One of them, U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub>, is ferromagnetic in spite of expected strong hybridization effects leading to nonmagnetic behavior. The band structure has been calculated using the local (spin) density approximation (L(S)DA) including generalized gradient corrections (GGA). In the spin polarized calculations also orbital polarization (OP) corrections were taken into consideration. *Ab initio* calculations were performed based on the full-potential local-orbital minimum-basis code FPLO. Total energy calculations for U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> showed that the magnetically ordered state is more stable than the nonmagnetic one. The calculated magnetic moment on the uranium atoms within the LSDA+GGA+OP approach gave a value equal to 1.2 μ<sub>B</sub>/atom.

Ab-initio calculations / Electronic band structure / Magnetic moments

### Introduction

Uranium ternaries U<sub>2</sub>T<sub>3</sub>M<sub>4</sub> (T = W, Mo, V; M = Si, Ge) crystallizing with U<sub>2</sub>Mo<sub>3</sub>Si<sub>4</sub>-type structures were synthesized and characterized by Bihan and Noël [1,2]. They reported that U<sub>2</sub>W<sub>3</sub>Si<sub>4</sub>, U<sub>2</sub>Mo<sub>3</sub>Si<sub>4</sub>, U<sub>2</sub>Mo<sub>3</sub>Ge<sub>4</sub>, and U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> crystallize with the space group P2<sub>1</sub>/c. The first three compounds do not show any magnetic order at low temperatures, while U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> undergoes a ferromagnetic transition at about 60 K [1,3]; the ordering moment calculated from the value of magnetization at 2 K is equal to 0.67 [3] or 0.68 μ<sub>B</sub> [1] per U ion.

The interatomic distance *d* between uranium atoms is one of the most important parameters influencing anomalous properties such as the Kondo effect and heavy fermion behavior in 5*f*-electron systems. Hill [4] has shown that for *d* < 3.5 Å, local moments are quenched due to interatomic *f*-*f* overlap, and this criterion is an empirical one often used as an indication of expected physical properties prior detailed investigations. The magnetic ordering temperatures as well as the magnetic moments seem to correlate with the *d* values. The *d* values of the above-listed compounds range from 3.348 Å for U<sub>2</sub>W<sub>3</sub>Si<sub>4</sub> to 3.429 Å for U<sub>2</sub>Mo<sub>3</sub>Ge<sub>4</sub>, *i.e.* they are very close to but slightly smaller than the Hill limit. U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> is one of several exceptions [5] having a *d* value smaller than the Hill limit, yet exhibiting magnetic ordering with a relatively high magnetic transition temperature.

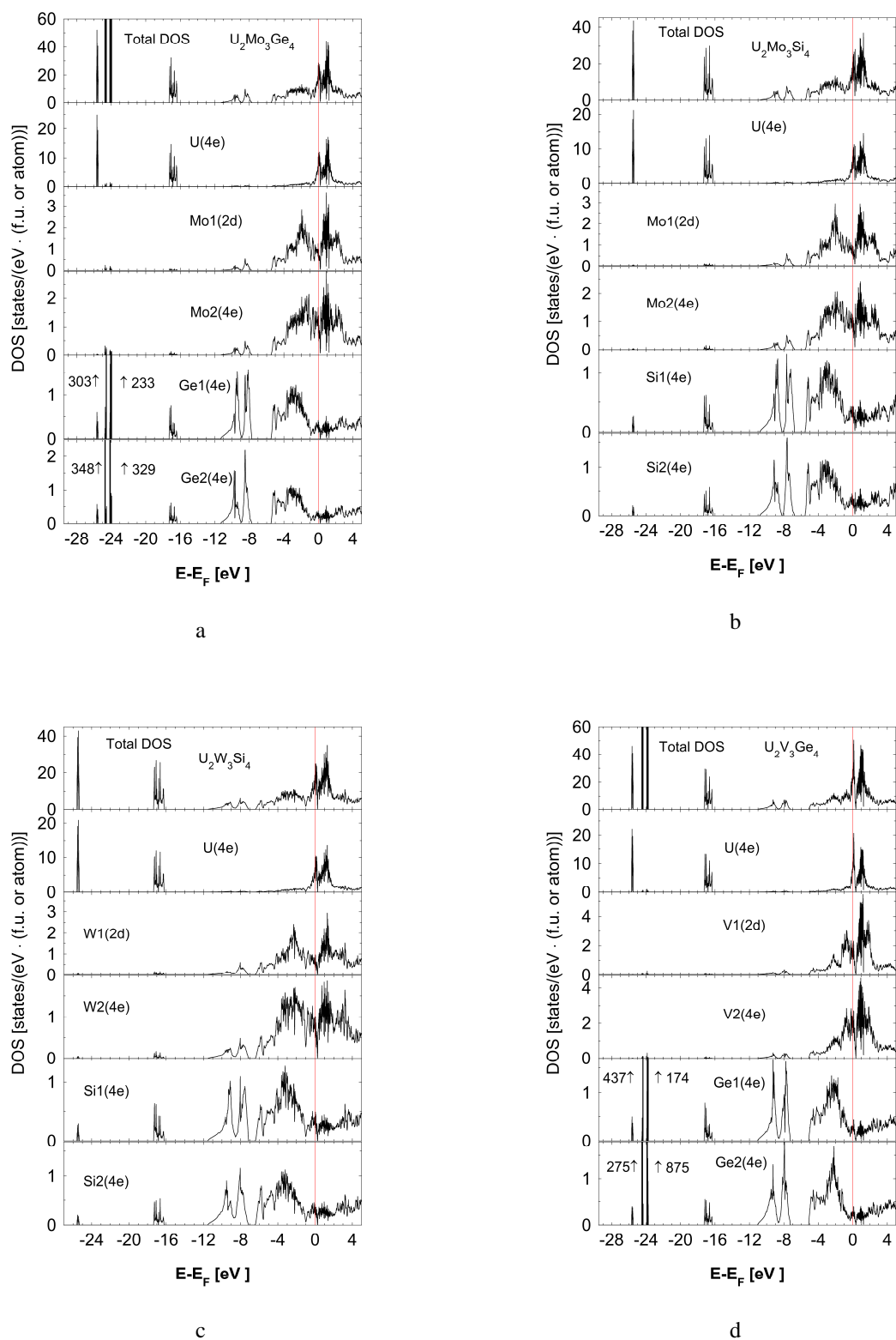
The aim of this work was to give insight into the electronic and magnetic structure of the U<sub>2</sub>T<sub>3</sub>M<sub>4</sub> compounds based on modern *ab initio* spin polarized band structure calculations.

### Details of the calculations

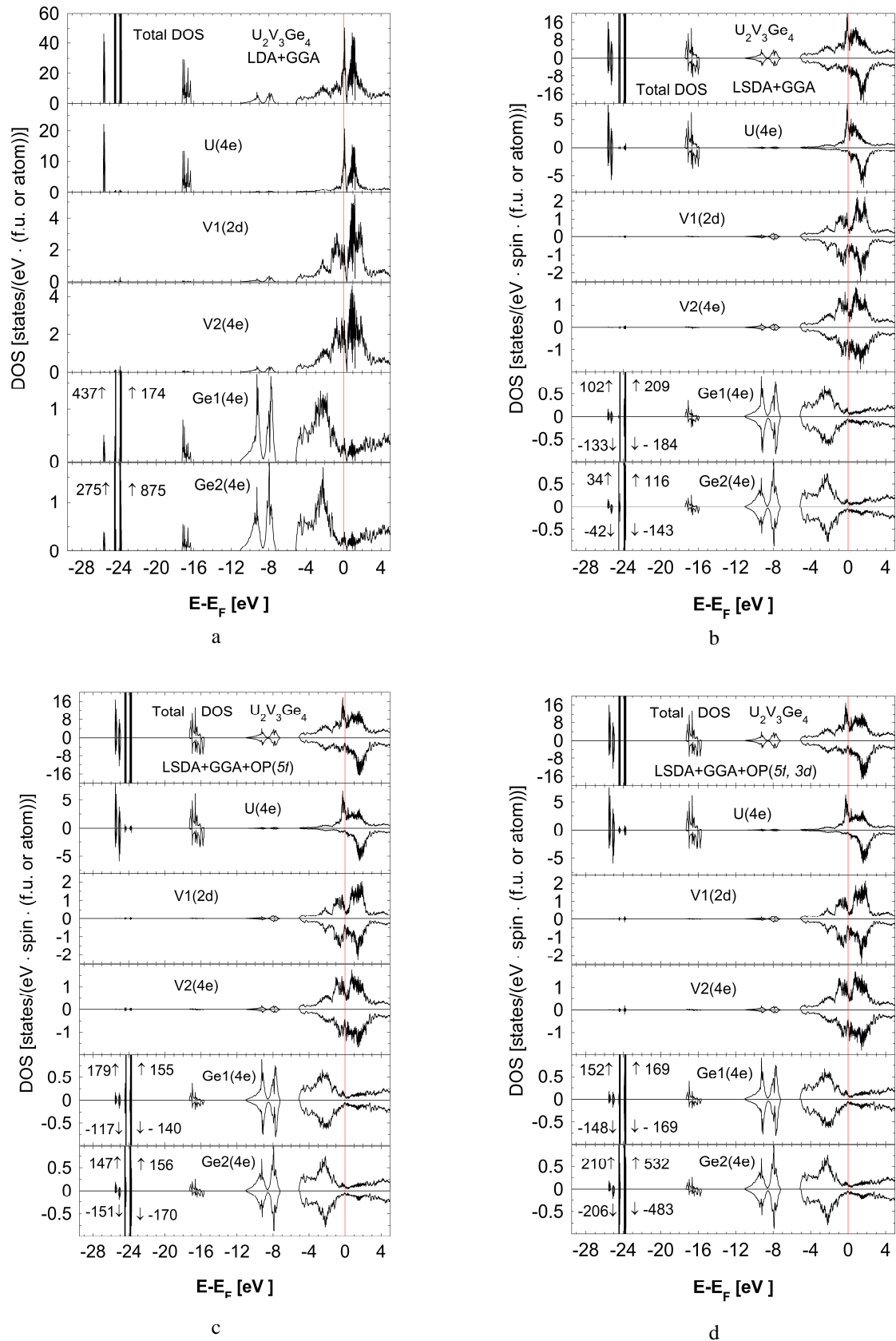
The band structure calculations were performed based on the full potential local-orbital minimum-basis code (FPLO [6], version 9.00-33 in the fully relativistic mode). We used the local (spin) density approximation (L(S)DA) with gradient corrections [7,8]. The generalized gradient approximation (GGA) was applied to the potential, parameterized in the form proposed by Perdew, Burke and Ernzerhoff [7,8]. Additionally we tested orbital polarization (OP) corrections [9-12]. The structures were not optimized and the calculations were performed for experimental lattice constants and atom coordinates [1-3]. For the Brillouin zone integration the tetrahedron method was used [13]. Two self-consistent criteria were used: the total energy was set equal to 2·10<sup>-8</sup> Ry and the charge to 10<sup>-6</sup> electrons.

### Results and discussion

The calculated band structure is presented in the form of DOS plots in Figs. 1 and 2. In the first place the



**Fig. 1** DOS plots (total and site projected) for  $U_2T_3M_4$  compounds calculated without spin polarization within the LDA+GGA approach.



**Fig. 2** Spin polarized DOS plots (total, spin and site projected) calculated for  $U_2V_3Ge_4$  within the LSDA+GGA approach, without OP corrections (b), and with OP corrections for the U(5f) (c) or the U(5f) and V(3d) states (d). In the first left panel (a) the LDA+GGA results are repeated for comparison.

**Table 1** Electronic and magnetic characteristics calculated for  $U_2T_3M_4$  ( $T = W, Mo, V$ ;  $M = Si, Ge$ ) compounds: densities of electronic states (DOS) at the Fermi level [states/(eV spin (f.u. or atom))] and local magnetic moments  $m$  [ $\mu_B$ /atom]. Calculations performed without (LDA+GGA) and with (LSDA+GGA) spin polarization, the latter also with orbital corrections (OP) to  $5f$  and  $3d$  states. The Sommerfeld coefficient  $\gamma_0$  [mJ/(mol K<sup>2</sup>)] in the linear term of the specific heat.

Atom (site)	$T = W$ ; $M = Si$	$T = Mo$ ; $M = Ge$	$T = Mo$ ; $M = Si$	$T = V$ ; $M = Ge$						
	LDA+GGA calculations				LSDA+GGA		LSDA+GGA+OP(5f)		LSDA+GGA+OP(5f+3d)	
	DOS				DOS	$m$	DOS	$m$	DOS	$m$
U(4e)	5.13	5.27	4.47	5.30	3.71/0.75	0.16	2.81/0.40	1.21	2.68/0.39	1.23
T(2d)	0.54	0.58	0.50	1.04	0.45/0.58	-0.26	0.33/0.36	0.48	0.30/0.36	0.49
T'(4e)	0.60	0.66	0.62	1.21	0.52/0.74	0.24	0.56/0.43	-0.23	0.53/0.42	-0.17
M'(4e)	0.26	0.18	0.23	0.15	0.08/0.07	-0.05	0.07/0.04	0.07	0.07/0.04	0.08
M''(4e)	0.28	0.17	0.21	0.15	0.09/0.07	-0.03	0.08/0.04	0.04	0.07/0.04	0.05
Total (per f.u.)	13.08	13.14	11.56	14.66	9.25/3.84	0.38	7.37/2.18	2.66	7.00/2.14	2.87
$\gamma_0$	61.7	70.0	54.5	69.1	30.9	–	22.5	–	21.6	–

results of calculations without spin polarization in Fig. 1 are shown. The presented spectra are composed of two parts: the first one between the Fermi energy ( $E_F = 0$ ) and -12 eV, and the second part below -12 eV. The higher binding spectra are formed by electrons treated in the calculations as semicore, where hybridization effects are weaker towards higher binding energies. These subbands are formed by U( $6p_{1/2}$ ) and U( $6p_{3/2}$ ) electrons located at around -25.5 and -17 eV, respectively. The U( $6p_{3/2}$ ) peak is much more broadened because of stronger hybridization than in the case of U( $6p_{1/2}$ ) electrons. Additionally, for systems containing germanium, two peaks, Ge( $3d_{3/2}$ ) and Ge( $3d_{5/2}$ ), are observed near -24 eV. The weak hybridization makes that these peaks are very narrow and high, approaching values beyond the presented panels. The valence bands have a characteristic gap approximately between -4 and -8 eV. The widths of these gaps are equal to 1–1.5 eV for the silicides and about 2 eV for the germanides. The subbands below -8 eV are formed mainly by Si( $3s$ ) and Ge( $4s$ ) electrons, and above the gap the main contribution is provided by Si( $3p$ ), Ge( $4p$ ), Mo( $3d$ ), W( $3d$ ), V( $3d$ ) electrons, as well as electrons located on uranium atoms:  $7s$ ,  $6d$ , and  $5f$ . Table 1 contains the DOS values at the Fermi level. The main contributions to the total DOS at the Fermi level are provided by electrons located on the uranium atoms (about 80%), especially  $5f$  electrons. The corresponding Sommerfeld coefficients ( $\gamma_0$ ) for the LDA+GGA calculations are between 54.5 and 70 mJ/(mol K<sup>2</sup>). Unfortunately, experimental values are not known. The spin polarized values of  $\gamma_0$  for the  $U_2V_3Ge_4$  compound are much lower (see Table 1). Fig. 2 presents spin projected DOS plots for the  $U_2V_3Ge_4$  compound, as well as nonmagnetic DOS's for comparison. The positions of the subbands are similar to those obtained for the nonmagnetic case, except for changes caused by band splitting leading to a magnetic solution with the spin

polarization  $P$  equal to 41%, determined by the expression  $P = (N\uparrow - N\downarrow)/(N\uparrow + N\downarrow) \times 100\%$ , where  $N$  is the density of states at the Fermi level for the spin direction marked by the arrow. Total energy calculations showed that the magnetic solution is more stable than the nonmagnetic one by about 13.88 mRy/f.u. The spin polarized DOS plots in Fig. 2 show that the main magnetic moment should be located on uranium atoms. Unfortunately the magnetic moment on the uranium atoms is equal to 0.16  $\mu_B$ /atom, only. This low value is the result of the cancellation of the spin and orbital moments, which have opposite directions: 1.95 and -1.79  $\mu_B$ /atom for the spin and orbital moment, respectively. This is a well known drawback of calculations based on the density functional theory, which give underestimated orbital magnetic moments. The most important *ab initio* approach, applied by us to remedy the discrepancy between the LSDA+GGA magnetic moments and the experimental ones, takes into account the so-called orbital polarization term as proposed by Brooks and Eriksson *et al.* [9, 10, 12], implemented in the FPLO method. In the first attempt the OP corrections were added to the  $5f$  states on uranium, and in the second one to the U( $5f$ ) and V( $3d$ ) states. In both cases the magnetic moment on uranium was overestimated: 1.21 and 1.23  $\mu_B$ /atom for LSDA+GGA+OP(5f) and LSDA+GGA+OP(5f+3d), respectively. The spin and orbital moments were equal to 2.15 and -3.36  $\mu_B$ /atom, respectively.

## Conclusions

In this paper the electronic structures of the  $U_2T_3M_4$  ( $T = W, Mo, V$ ;  $M = Si, Ge$ ) compounds have been calculated by the FPLO method. The main results are summarized as follows:

- the U(5f) electrons have delocalized character, they form a band and together with electrons of the 3d elements provide the main contribution to the densities of states in the range near the Fermi level;
- total energy calculations for U<sub>2</sub>V<sub>3</sub>Ge<sub>4</sub> showed that a magnetically ordered state is more stable than the nonmagnetic one, in spite of inter-uranium distances below the Hill limit;
- *ab initio* calculations within the LSDA+GGA approach gave too small values for the magnetic moment (0.16 μ<sub>B</sub>/atom) on the uranium atoms; use of orbital polarization corrections led to an overestimation of the magnetic moment, which now reached the value of 1.2 μ<sub>B</sub>/atom, too high compared with the experimental value 0.68 μ<sub>B</sub>/atom.

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