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Magnetic Properties of the U_5Ge_4 Compound Based on *Ab initio* Calculations

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U_5Ge_4 crystallizes in a hexagonal Ti_5Ga_4 type structure with two inequivalent crystallographic sites occupied by uranium atoms. The band structure calculations were performed by the full-potential local-orbital minimum basis band structure code. The calculations showed that on both types of uranium atoms small magnetic moments are formed and their values are equal to 0.08 and 0.15 μ_B/atom, respectively.

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1. Introduction

Uranium germanides have been widely investigated both experimentally and theoretically because of their interesting physical properties. The recently reinvestigated phase diagram of the U–Ge system consists of six compounds [1]. U_5Ge_4 crystallizes in a hexagonal Ti_5Ga_4 type structure with $P6_3/mcm$ space group [2]. The unit cell contains 18 atoms: uranium atoms occupy two inequivalent sites, 4d and 6g, and germanium atoms also two sites: 6g and 2b. Magnetic susceptibility investigations showed a nearly temperature independent paramagnetic behavior down to 2 K [1, 2]. Lack of magnetic order was explained by a direct overlap between $5f$ shells of uranium U(4d) along the c axis, according to a short distance between each U(4d) atoms, and delocalization of $5f$ electrons of U(6g) atoms probably occurring via hybridization effects with the sp shells of the surrounding germanium atoms. The interatomic distances between uranium atoms are as follows [2]: U(4d)–U(4d) 2.931 Å, U(4d)–U(6g) 3.484 Å and U(6g)–U(6g) 3.832 Å. This means that the distances are alike below and above so-called Hill limit [3] equal to *ca.* 3.4 Å, and one can expect magnetic moments localized at least on U(6g) atoms. Earlier calculations [4], based on a not fully relativistic method, suggested forming of magnetic moments on uranium atoms. These total energy calculations reported ferromagnetic state as more stable than nonmagnetic one.

In this paper the problem of magnetic moments forming on uranium atoms will be analyzed based on *ab initio* fully relativistic calculations.

2. Computational details

In order to study electronic structure of U_5Ge_4 we used the full-potential local-orbital (FPLO) method [5] based on the local spin density approximation (LSDA) [6]. The calculations were carried out for the hexagonal structure with 18 atoms per unit cell (two formula units) and experimental values of the lattice constants [2]. For the calculations we assumed the following configurations of atoms: core (up to $5p$ electrons) + semi core ($5d6s$) + valence electrons ($6p7s7p6d5f$) for uranium atoms, core (up to $3p$ electrons) + valence electrons ($3d4s4p$) for Ge atoms. The calculations were performed for the reciprocal space mesh containing 270 points within the irreducible wedge of the Brillouin zone using the tetrahedron method [7] for integrations. The LSDA exchange-correlation potential was assumed in the form proposed by Perdew and Wang [8]. The self-consistent criterion was equal to 2×10^{-8} Ry for the total energy.

3. Results and discussion

The electronic structures of U_5Ge_4 for nonmagnetic and magnetic cases were calculated using the FPLO method in the fully-relativistic mode. The relativistic effects are very important for uranium compounds and the full potential approach gives much more reliable values of the total energy than in the atomic sphere approximation used in earlier calculations [4]. Previous calculations [4] reported magnetically ordered state of the U_5Ge_4 as more stable than the nonmagnetic one, and the difference of total energies $\Delta = E_{FM} - E_{NM}$ was equal to 1.7 Ry/f.u. Present calculations gave significantly less value equal to 5×10^{-4} Ry/f.u.

The densities of electronic states (DOS) presented in Figs. 1 and 2 are calculated without and with spin polarization. These two approaches were used because magnetic susceptibility investigations showed a nearly temperature independent paramagnetic behavior down to 2 K [1, 2], but the isostructural stannide U_5Sn_4 [9]

and antimonide U_5Sb_4 [10], having slightly larger interatomic distances than U_5Ge_4, exhibit ferromagnetic ordering. The magnetic moments for U_5Sb_4 [10] compound for U(4d) and U(6g) atoms are equal to about 1.6 and 1.7 μ_B/atom, respectively.

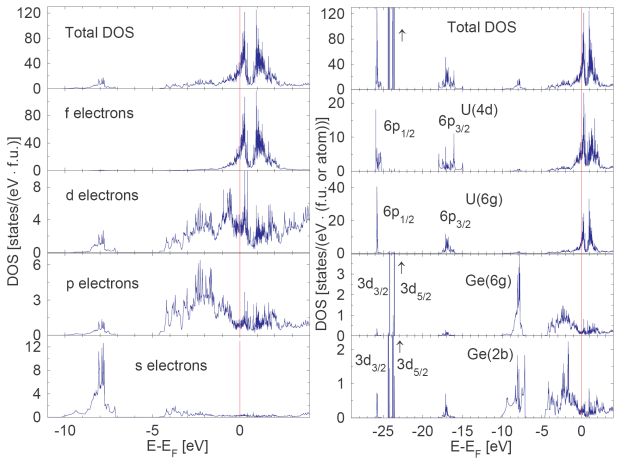

Fig. 1. DOS plots for nonmagnetic U_5Ge_4. Left part: total and l-decomposed partial DOS plots. Right part: site projected DOS plots.

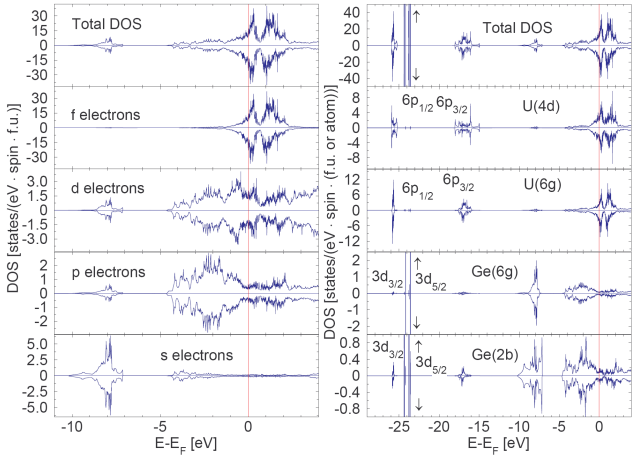

Fig. 2. DOS plots for magnetic U_5Ge_4. Left part: total and l-decomposed partial DOS plots. Right part: site projected DOS plots.

The valence band can be divided into three parts:

a) around 15–21 eV below the Fermi level (E_F) formed mainly by 6p electrons of the uranium atoms and 3d of germanium ones;

b) around 7–10 eV below E_F formed mainly by Ge(4s) electrons;

c) between 4.5 and 0 eV below E_F, formed by Ge(4p) and U(6d + 5f) electrons.

The DOS plots in the first range of binding energy show completely different character of U(6p) and Ge(3d) electrons. The Ge($3d_{3/2}$) and Ge($3d_{5/2}$) electrons almost do not take part in hybridization. They form very narrow bands and the peaks in Figs. 1 and 2 (right parts) are very high. The arrows mean that maxima of the peaks are out of scale. In the magnetic case, the maxima reach the following values:

— for Ge on 6g site, $3d_{3/2}$ electrons: 260 for spin up and 273 for spin down;

— for Ge on 6g site, $3d_{5/2}$ electrons: 316 for spin up and 331 for spin down;

— for Ge on 2b site, $3d_{3/2}$ electrons: 196 for spin up and 164 for spin down;

— for Ge on 2b site, $3d_{5/2}$ electrons: 546 for spin up and 436 for spin down; (all above values are expressed in [states/(eV spin f.u.)]).

The behavior of 6p electrons on uranium atoms is very interesting because of interatomic distances: U(4d)–U(4d) below and U(6g)–U(6g) above the Hill limit. In the case of U(4d) atoms, shorter interatomic distances intensify hybridization: the DOS peaks are smaller, more broadened, and the bands are wider.

Similar behavior is observed for 4s electrons located on Ge atoms, range 7–10 eV below E_F, where interatomic distances are: Ge(6g)–Ge(6g) is equal to 3.622 Å, and Ge(2b)–Ge(2b) 2.931 Å. The Ge(4s) electrons on 2b sites are more receptive to hybridization than the Ge(4s) ones on 6g sites. They form subband about twice wider than the Ge(4s) electrons on 6g sites.

The main contribution to the total DOS at the Fermi level is provided by U(5f) electrons, about 86% of the total DOS. The values of DOS($E = E_F$) are collected in Table. They correspond to the Sommerfeld coefficient in the electron term of the specific heat: $\gamma_0^{PM} = 70$ and $\gamma_0^{FM} = 82$ mJ/(mol K^2) for nonmagnetic and magnetic case, respectively. Total energy calculations showed that the magnetically ordered state of the U_5Ge_4 is more stable than the nonmagnetic one but magnetic moments on uranium atoms are small because of opposite signs of spin and orbital moments (see Table). The calculated magnetic moments are equal to: 0.08, 0.15, 0.02, and 0.02 μ_B/atom for U(4d), U(6g), Ge(6g), and Ge(2b), respectively. Similar (0.09 and 0.15) values for moments on uranium atoms were obtained using in our calculations the orbital polarization based on Eriksson et al. [11] scheme. Small magnetic moments on Ge atoms are formed because of polarization of their external shells of electrons.

We see that the U(4d) atom, with the shortest inter-uranium distances, has significantly reduced moment comparing with the moment of the U(6g) atom. For U(4d) atoms, the hybridization effects reduce the heights of 5f and 6p DOS plots, and the appropriate bands are more broadened than for U(6g) ones. Similar results were

TABLE

Densities of electronic states (DOS) at the Fermi level [states/(eV spin (f.u. or atom))] and local magnetic moments m (t:total, s:spin, o:orbital). The signs ↑ and ↓ describe spin directions for magnetic case, up and down, respectively. The paramagnetic case is described by PM.

Type of DOS	Total and partial DOS (per f.u.)	Atom (position)	Site--projected DOS (per atom)	m [μ_B/atom]
Total DOS	↑ 12.81	U(4d)	↑ 2.51	s:-0.03
	↓ 21.92		↓ 3.42	o: 0.11
	PM 14.85		PM 2.51	t: 0.08
Total DOS	↑ 0.14	U(6g)	↑ 2.46	s:-0.72
s-electrons	↓ 0.19		↓ 4.90	o: 0.87
	PM 0.13		PM 3.17	t: 0.15
Total DOS	↑ 0.53	Ge(6g)	↑0.09	s: 0.02
p-electrons	↓ 0.53		↓0.09	o: 0.00
	PM 0.44		PM 0.07	t: 0.02
Total DOS	↑1.75	Ge(2b)	↑0.14	s: 0.02
d-electrons	↓1.75		↓0.11	o: 0.00
	PM 1.40		PM 0.11	t: 0.02
Total DOS	↑10.39			
f-electrons	↓19.45			
	PM 12.88			

observed earlier [4] but the calculations were not performed in fully relativistic mode and only spin magnetic moments were available.

Taking into account band structure calculations and experimental results (also for isostructural antimonide U_5Sb_4 and stannide U_5Sn_4) one can conclude that U_5Ge_4 compound can present magnetic order with small moments formed on uranium atoms (especially U(6g) ones) and according to susceptibility measurements the Curie temperature should be below 2 K.

Acknowledgments

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