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Electronic structure of U_5Ge_4

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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 method of tight binding version of the linear muffin-tin orbital in the atomic sphere approximation (TB-LMTO ASA). The calculations showed that both types of uranium atoms can be magnetically ordered and then their spin magnetic moments are equal to 0.5 and –1.2 μ_B/atom, respectively.

Key words: *uranium compound; electronic structure; magnetic moment*

1. Introduction

Uranium germanides have been widely investigated both experimentally and theoretically because of their interesting anomalous physical properties. The recent thorough reinvestigation of the U–Ge system has finally established the existence of six compounds with the chemical formulae U_5Ge_4, UGe, U_3Ge_5, UGe_2, UGe_3 and UGe_{2-x}, where $0.30 < x < 0.35$ [1]. U_5Ge_4 crystallizes in a hexagonal Ti_5Ga_4 type structure with $P63/mcm$ space group [2]. The unit cell has a complex structure and 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 behaviour 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) atom, 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 below and above so-called Hill limit [3] equal to ca. 3.4 Å, and one can expect magnetic moments lo-

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cated on U(6g) atoms. A similar situation was observed in UGe [4], where for one of three types of uranium atoms, the inter-uranium distances were below the Hill limit, and for remaining ones – above the Hill limit, which strongly influenced their magnetic moments.

The aim of this paper is to present the electronic structure of U_5Ge_4 for both nonmagnetic and a hypothetical magnetic case.

2. The method of calculations and results

The electronic structures for nonmagnetic and magnetic cases were calculated using the spin-polarized tight-binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [5, 6].

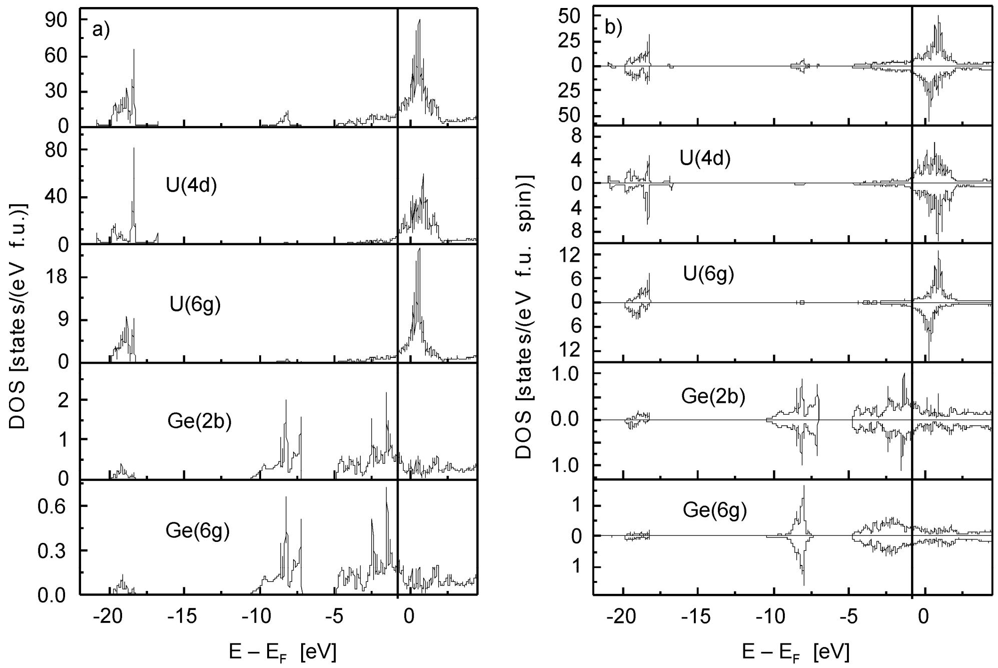

Fig. 1. The total (per f.u.) and site projected (per atom) densities of electronic states (DOS) for U_5Ge_4 in the paramagnetic state (a) and a hypothetical magnetic state (b)

The overlap volume of the muffin-tin spheres is about 9%. The standard combined corrections [5] for overlapping were used to compensate errors due to the ASA. The experimental values of the lattice constants [2] were used in the calculations. Spin -orbit interactions were taken into account in the form proposed by Min and Jang [7]. The exchange correlation potential was assumed in the form proposed by von Barth and Hedin [8]. Self-consistent calculations were carried out for 396 *k*-points in the irreducible wedge (1/24) of the Brillouin zone. For integration over the Brillouin zone the tetrahedron method was used [9]. The iterations were repeated until the total energies of the consecutive iteration steps were the same within the error of 0.01 mRy.

The X-ray photoemission spectroscopy (XPS) is a very useful tool to confirm the band structure calculations. To the best of our knowledge, up to now, spectra of U_5Ge_4 have not been recorded. We present computed photoemission spectra. The method used here consists in weighting the density of states (DOS) with appropriate atomic cross sections for photon scattering [10] and applying a convolution with a Gaussian function which accounts for a finite experimental resolution δ. In our case, the photon energy is equal to 1486.6 eV (AlK$_\alpha$ source) and the parameter δ is equal to 0.3 eV.

The densities of electronic states (DOS) are presented in Fig. 1 for nonmagnetic and magnetic cases. In both cases, the valence bands can be divided into three parts:

- around 18–20 eV below the Fermi level (E_F) formed mainly by 6p electrons of the uranium atoms;
- around 7–10 eV below E_F formed mainly by Ge(4s) electrons;
- between 5 and 0 eV below E_F, formed by Ge(4p) and U(6d+5f) electrons.

Table 1. Spin projected (↑,↓) densities of electronic states (DOS [states/(eV spin (f.u. or atom))]) at the Fermi level for U_5Ge_4 in a nonmagnetic state (PM) and a magnetic one (FM)

Type of DOS	Spin direction	Total and l-decomposed DOS (per f.u.)		Atom (position)	Spin direction	Site-projected DOS (per atom)	
		PM	FM			PM	FM
Total	↑	–	10.65	U(4d)	↑	–	2.91
	↓	–	12.12		↓	–	1.07
	↑+↓	23.32	22.77		↑+↓	3.67	3.98
Total for s electrons	↑	–	0.14	U(6g)	↑	–	1.37
	↓	–	0.06		↓	–	3.15
	↑+↓	0.21	0.20		↑+↓	5.01	4.52
Total for p electrons	↑	–	0.61	Ge(6g)	↑	–	0.19
	↓	–	0.36		↓	–	0.11
	↑+↓	0.85	0.97		↑+↓	0.22	0.30
Total for d electrons	↑	–	1.91	Ge(2b)	↑	–	0.15
	↓	–	1.00		↓	–	0.14
	↑+↓	2.56	2.91		↑+↓	0.27	0.29
Total for f electrons	↑	–	7.98				
	↓	–	10.72				
	↑+↓	19.69	28.72				

The main contribution to the total DOS at the Fermi level is provided by U(5f) electrons. The values of DOS ($E = E_F$) are collected in Table 1. Total energy calculations showed that the magnetically ordered state of the U_5Ge_4 is more stable than the nonmagnetic one. The isostructural antimonide U_5Sb_4 [11] and stannide U_5Sn_4 [2], having slightly larger interatomic distances than U_5Ge_4, exhibit ferromagnetic ordering. In the case of U_5Ge_4, the calculated spin magnetic moments are equal to: 0.50, –1.21, 0.01, and 0.03 μ_B/atom for U(4d), U(6g), Ge(6g), and Ge(2b), respectively. 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) atoms.

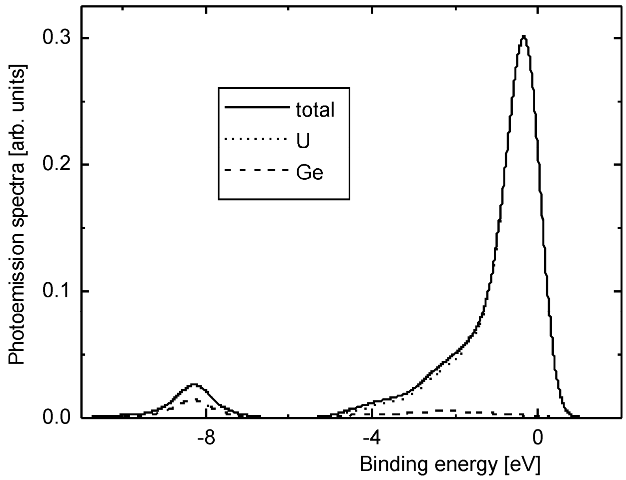

Fig. 2. X-ray photoemission spectra of U_5Ge_4

The calculated photoemission spectra are presented in Fig.2. The spectra were calculated based on the paramagnetic DOS functions since the system is nonmagnetic down to 2 K. The total spectrum is dominated by one main peak located close to the Fermi level. Ge atoms provide only small contribution to the total spectrum. The significant uranium contribution comes from considerable contribution of DOS function and large value of cross sections for 5f electrons.

3. Conclusions

In this paper, the electronic structure of U_5Ge_4 has been calculated by the TB-LMTO method. The calculations were performed with and without spin polarization. The main results are summarized as follows:

The results of calculations of the band structure show that the magnetically ordered state of U_5Ge_4 is more stable than the nonmagnetic one.

The U(5f) bands dominate the densities of states near the Fermi level on calculated X-ray photoemission spectrum.

The values of spin magnetic moments on uranium atoms are strongly dependent on the local environments and are equal to 0.50 and –1.21 μ_B/atom for U(4d) and U(6g) atoms, respectively.

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