The Electronic and Magnetic Properties of UGe Compound

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The UGe system crystallizes in the orthorhombic ThIn-type structure. The uranium atoms occupy three crystallographic sites with interatomic U–U distances like below and above the Hill limit. The band structure has been calculated by using the density functional theory and generalized gradient approximation. Ab initio calculations were performed based on the full-potential local-orbital minimum-basis code. Calculations showed that all three types of uranium atoms are magnetically ordered with antiparallel alignment of the magnetic moments. For uranium atoms with an interatomic distance below the Hill limit magnetic moments are significantly reduced due to hybridization effects.

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1. Introduction

The recent reinvestigation of the U–Ge system has finally established existence of six compounds with the chemical formulas \( \text{U}_5\text{Ge}_4 \), \( \text{UGe} \), \( \text{U}_3\text{Ge}_5 \), \( \text{UGe}_2 \), \( \text{UGe}_3 \) and \( \text{UGe}_{2−x} \) (existing in a homogeneity range of \( 0.30 < x < 0.35 \)) [1]. The existence of the uranium monogermanide UGe was first time reported by Alcock and Grieveson [2]. The UGe compound crystallizes in the orthorhombic ThIn-type structure (Pbnm space group) [3]. Both uranium and germanium atoms occupy three crystallographic positions: U1(4d), U2(4d), U3(4c), and Ge1(4d), Ge2(4d), Ge3(4c). The U3–U3 distance between uranium U3 atoms equal to 2.92 Å is below the Hill limit (\( \sim 3.4 \) Å). The U3 atoms form metallic chains along the \( c \) axis. Magnetic measurements indicate the Curie–Weiss type behavior down to 1.7 K [3]. The average effective moment is equal to 2.47 \( \mu_B/\text{U atom} \). There is no magnetic ordering transition down to 1.7 K. Earlier calculations [4] showed that all three types of uranium atoms are magnetically ordered.

The aim of this work is to give insight into the magnetic structure of the UGe compound based on the modern \textit{ab initio} spin polarized band structure calculations.

2. Details of calculations

The full potential local-orbital minimum-basis code (FPLO [5], v. 9.00-33) was employed. The DFT calculations were performed without and with the orbital polarization (OP) correction [6]. We used experimental lattice constants and the Wyckoff positions [3]. The unit cell contains 24 atoms. The generalized gradient approximation (GGA) [7] was used to the potential parameterized in the form proposed by Perdew et al. [7]. The tetrahedron method was employed for the Brillouin-zone integration [8]. The self-consistent criterion for the total energy was equal to \( 10^{-8} \) Ha, a criterion for charge was equal to \( 10^{-6} \) electrons.

3. Results and discussion

The results of calculations without spin polarization are shown in Fig. 1. The valence bands have gap between −4.7 and −6.7 eV. The subbands between −10.8 and −8 eV are formed mainly by Ge(4s) electrons. Above the gap the main contribution is provided by Ge(4p) and U(7s, 6d, 5f) electrons. The higher binding spectra are formed by U(6p_{1/2}) and U(6p_{3/2}) electrons located at −25.5 and −17 eV. Because of stronger hybridization the U(6p_{3/2}) peak is more broadened than U(6p_{1/2}). At −24 eV are two very narrow and high peaks: Ge(3d_{3/2}) and Ge(3d_{5/2}). U(5f) electrons provide the main contribution to the total DOS at the Fermi level (about 95%) (see Table). The Sommerfeld coefficient \( \gamma_0 \) is equal to 19.4 mJ/(mol K²). Unfortunately experimental value is not known.

The spin polarized values of \( \gamma_0 \) are much lower. Total energy calculations showed that magnetic solution is more stable by about 46.4 meV/f.u. Spin projected DOS...
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TABLE

DOS at the Fermi level [states/(eV spin (f.u. or atom))] and local magnetic moments \( m \) [\( \mu_B \)/atom]. Calculations performed without (NSP) and with (SP) spin polarization, the latter also with orbital corrections (OP) applied to 5f states. The Sommerfeld coefficient \( \gamma \) [mJ/(mol K²)] in the linear term of the specific heat.

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>DOS [states/(eV spin)]</th>
<th>m</th>
<th>SP+OP DOS [states/(eV spin)]</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1(4d)</td>
<td>4.68/3.32/0.99/0.29</td>
<td>0.05</td>
<td>2.22/0.71</td>
<td>−1.42</td>
</tr>
<tr>
<td>U2(4d)</td>
<td>4.31/1.18/4.36/0.75</td>
<td>0.75</td>
<td>1.21/3.70</td>
<td>1.48</td>
</tr>
<tr>
<td>U3(4c)</td>
<td>2.77/3.39/2.31/0.02</td>
<td>−0.02</td>
<td>2.21/0.92</td>
<td>−0.38</td>
</tr>
<tr>
<td>Ge1(4d)</td>
<td>0.20/0.14/0.18/0.02</td>
<td>−0.02</td>
<td>0.12/0.18</td>
<td>−0.08</td>
</tr>
<tr>
<td>Ge2(4d)</td>
<td>0.16/0.15/0.14/0.03</td>
<td>0.03</td>
<td>0.17/0.16</td>
<td>−0.03</td>
</tr>
<tr>
<td>Ge3(4c)</td>
<td>0.24/0.19/0.24/0.01</td>
<td>−0.01</td>
<td>0.17/0.22</td>
<td>−0.01</td>
</tr>
<tr>
<td>total (per f.u.)</td>
<td>4.12/2.79/2.75/0.09</td>
<td>2.21/1.96</td>
<td>−0.15</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>19.4/13.1/9.8/–</td>
<td>–</td>
<td>9.8/–</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. The spin polarized (SP-GGA) DOS plots (total and site projected) within the GGA approach, also including OP corrections to the 5f states (SP-GGA+OP).

The most important ab initio approach, applied by us to improve discrepancy between the GGA magnetic moments and experimental ones, takes into account so-called orbital polarization term as proposed by Eriksson et al. [6], implemented in FPLO code. Results are presented in the right part in Fig. 2. The OP corrections were added to the 5f states on uranium atoms. In all uranium atoms magnetic moments increased. The resultant moments are collected in Table. The OP approach gives moments on U3 atom much lower than for U1 and U2.

In spite of use more advanced FPLO method than in our previous work [4] we have to be aware of static DFT limitations in describing real ground state, which can be very much influenced by the pronounced fluctuations of magnetic moments (see for example paper by Prokeš et al. [9]). Such complex ground state can be better described by the dynamical mean field theory (DMFT) [10].

4. Conclusions

Presented results of the spin polarized band structure calculations, within GGA and GGA+OP approach, for UGe compound showed that on all three types of uranium atoms magnetic moments are formed. The moments on U1 and U2 atoms have an antiparallel alignment. The moment on U3 atom is reduced because of the short U3–U3 distance, which leads to the overlap of the corresponding 5f orbitals. The results can clarify the low value of the effective magnetic moment obtained by the susceptibility measurements.

Acknowledgments

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References