
The Electronic and Magnetic Properties of the USn_2 Compound

A. SZAJEK

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

(Received August 27, 2003; revised version April 20, 2004)

The *ab initio* self-consistent calculations were performed for USn_2 compound, which crystallizes in the ZrGa_2 -type structure ($Cmmm$ space group). The tight binding linear muffin-tin orbital method in the atomic sphere approximation was used in the calculations. The spin-polarized calculations confirmed the antiferromagnetic order in the USn_2 system. The magnetic moment is predominantly located on the uranium atoms and is formed mainly by the f electrons. The three types of Sn atoms may be treated as non-magnetic.

PACS numbers: 71.20.-b, 75.25.+z

1. Introduction

Recently uranium compounds have attracted interest because of many interesting properties such as the Pauli paramagnetism, spin fluctuations, heavy fermions, magnetic ordering, or superconductivity. Wide range of properties in these compounds is caused by the uranium $5f$ electrons, which show an intermediate character between the localized $4f$ electron system and itinerant character of $3d$ electrons. The way to understand these properties is systematic studying of the phase diagrams of the binary phases, where the same atoms located in different crystallographic lattices lead to unique phenomena.

The first reference on the binary U-Sn was by Treick et al. [1]. The existence of three binary compounds was reported: USn_3 , U_3Sn_5 , and U_3Sn_2 . This paper was a basis for a tentative phase diagram proposed by Sheldon et al. [2]. These investigations led to conclusion that compounds such as U_3Sn_7 , USn_2 , U_5Sn_4 , and USn reported by Sari et al. [3] are not truly equilibrium phases. The comprehensive

work by Palenzona and Manfrinetti [4], in which the techniques of differential thermal analysis, metallographic analysis, X-ray diffraction, and electron microscopy were employed, has removed the uncertainty in this matter. The following intermediate, homogeneous phases have been confirmed: U_5Sn_4 , USn , USn_2 , U_3Sn_7 , and USn_3 . The U_3Sn_5 and U_3Sn_2 systems were found to be non-homogeneous. The latest reinvestigation of the structural chemistry of the binary stannides [5] confirmed the following phases reported earlier [4]: USn_3 (AuCu₃-type), U_3Sn_7 (Ce_3Sn_7 -type), USn_2 (ZrGa_2 -type), USn (ThIn-type), and U_5Sn_4 (Ti_5Ga_4 -type).

The magnetic measurements [5, 6] showed that U_3Sn_7 and USn_2 are antiferromagnets, USn and U_5Sn_4 are ferromagnets and USn_3 is a spin fluctuating system. The temperatures of magnetic ordering are in the range between 49 K and 80 K [5, 6]. A comparison of this behaviour to that of the isostructural binary germanides reveals an interesting evolution of magnetic interactions connected to the hybridization of U(5*f*) electrons with those of the ligands (Sn, Ge). The antiferromagnetic order was confirmed for U_3Sn_7 and USn_2 by neutron diffraction [7].

As a first step toward an understanding of the electronic states in the whole temperature range, it is important to clarify the ground state properties of these compounds. Recently developed theoretical methods to carrying out reliable qualitative calculations of energy band structures are very powerful tools. However, it is a big challenge to calculate band structure of 5*f* electron systems. The degree of localization of the U(5*f*) states is not known and analysis of interuranium distances indicates possible different degree of localization of 5*f* electrons. Till now, for binary U–Sn systems, the band structure calculations have been reported for two compounds: USn_3 [8–11] and USn [12]. The first compound has simple unit cell (AuCu₃-type) but the problem was to take into account many body effects responsible for large enhancement in the specific heat coefficient, which in the case of USn_3 is about seven times larger than for UGe_3 . The second compound, USn (ThIn-type structure), has much more complex unit cell: uranium and tin atoms each occupy three crystallographic positions marked as 4d, 4d, and 4c sites. In this structure the U(4c) atoms form metallic chains running along *c* axis, with interatomic U(4c)–U(4c) distance of 3.10 Å, which is close to the Hill limit, and the remaining interatomic distances between uranium atoms are well above the limit. USn orders ferromagnetically with an ordered moment of 1.2 μ_{B}/U [5]. Because of the short U(4c)–U(4c) distance and expected hybridization between *f* states and the conduction-band electron states it was interesting to know if this uranium sublattice is also magnetically ordered. In the isostructural germanide UGe situation was similar but in this compound U(4c)–U(4c) distance is shorter, about 2.9 Å, and calculated spin magnetic moment is reduced to about 0.2 μ_{B}/U [13]. The rest of U atoms have magnetic moments about nine times larger and they order antiferromagnetically. In the case of USn , the calculations showed that magnetic moments on U atoms order ferromagnetically, and the spin moments have similar values (2.7–2.9 μ_{B}/U atom), even in the case of U(4c) atoms.

The USn_2 compound has relatively tin-rich composition and orders antiferromagnetically. Its isostructural equivalent UGe_2 orders ferromagnetically at ambient pressure, and T_C decreases under pressure, vanishing at about 1.6 GPa [14]. Around 1 GPa, Saxena et al. [15] have found that UGe_2 becomes superconducting while remaining ferromagnetic ($m \approx 1 \mu_B/U$ atom) providing a novel example of coexistence of the superconductivity and ferromagnetism. The band calculations performed by Shick and Pickett [16] reproduced the magnitude of the observed magnetic moment and the magnetic anisotropy.

The aim of this paper is to calculate the electronic structure of the USn_2 compound and compare the obtained results with the experimental ones.

2. Method of calculations

The electronic band structure was calculated by the tight-binding linear muffin-tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [17, 18]. The neutron diffraction [7] experimental values of the lattice parameters were assumed for computations. In the crystal structure of USn_2 uranium atoms occupy one position 4j and tin atoms occupy three crystallographic positions marked as 4i, 2a, and 2c sites (see Fig. 1). The unit cell accommodates four formula units, the positions of atoms are given in Table I. In the ASA the volume of the unit cell is divided into the Wigner-Seitz (W-S) atomic spheres of the different radii, which are collected in Table I. The average Wigner-Seitz radius is 1.825 Å.

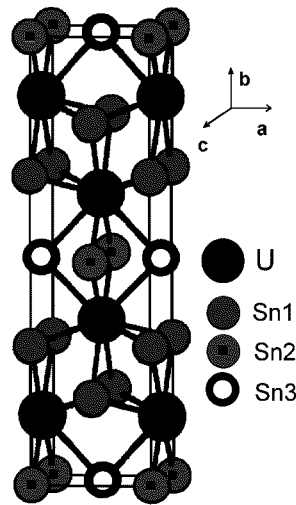


Fig. 1. The crystallographic unit cell of USn_2 compound.

TABLE I

Structural parameters of USn_2 compound (orthorhombic, ZrGa_2 -type, space group: $Cmmm$).

Atom (site)	x	y	z	S_j [Å]
U(4j)	0.0	0.1477(4)	0.5	1.962
Sn1(4i)	0.0	0.3229(5)	0.0	1.742
Sn2(2a)	0.0	0.0	0.0	1.762
Sn3(2c)	0.5	0.0	0.5	1.744

The starting atomic configurations were assumed as core $+6p^65f^36d^17s^2$ for U, and core $+5s^25p^2$ for Sn atoms. The overlap volume of muffin-tin spheres for the chosen W–S radii S_j was 9.67%. The standard combined corrections for overlapping W–S spheres [17] were applied to compensate the ASA errors. The fully relativistic treatment was used for the core electrons and for the valence electrons the scalar relativistic approximation supplemented by the spin–orbit effects taken into account within the Min and Jang scheme [19] was adopted. The von Barth–Hedin [20] exchange–correlation potential was used. The self-consistent calculations were performed for 1221 k -points in the irreducible wedge (1/8) of the Brillouin zone. The iteration procedure was ended when the self-consistency within the 0.01 mRy error was achieved. For the integration in the k -space the standard tetrahedron method was used [21].

3. Results and discussion

The spin polarized band structure calculations were performed using the TB LMTO ASA method for double unit cell along c axis, as it was suggested by neutron diffraction (see Fig. 3 in [7]). The uranium atoms in distinct cells were formally treated as different types of atoms, the calculations for them were performed independently up to self-consistency. We also obtained solutions for ferromagnetic order and antiferromagnetic order with antiparallel alignment within single unit cell. In both cases the total energies were higher than for the case described by the neutron diffraction. The presented below results of calculations will concern only this situation.

The calculated electronic structure of USn_2 gave density of states (DOS) plots presented in Figs. 2 and 3. The total DOS in Fig. 2A is decomposed into contributions from s , p , d , and f electrons in respective panels (let us note the different vertical scales). Site projected DOS plots are presented in Fig. 2B.

In the total DOS a few characteristic features can be observed. The two subbands located between 17.9 and 19.5 eV below the Fermi level (taken as $E_F = 0$) is due to the U p electrons (95.6%) with small contributions from Sn atoms (s and p electrons), which are the nearest neighbours of the U atoms. The distances between

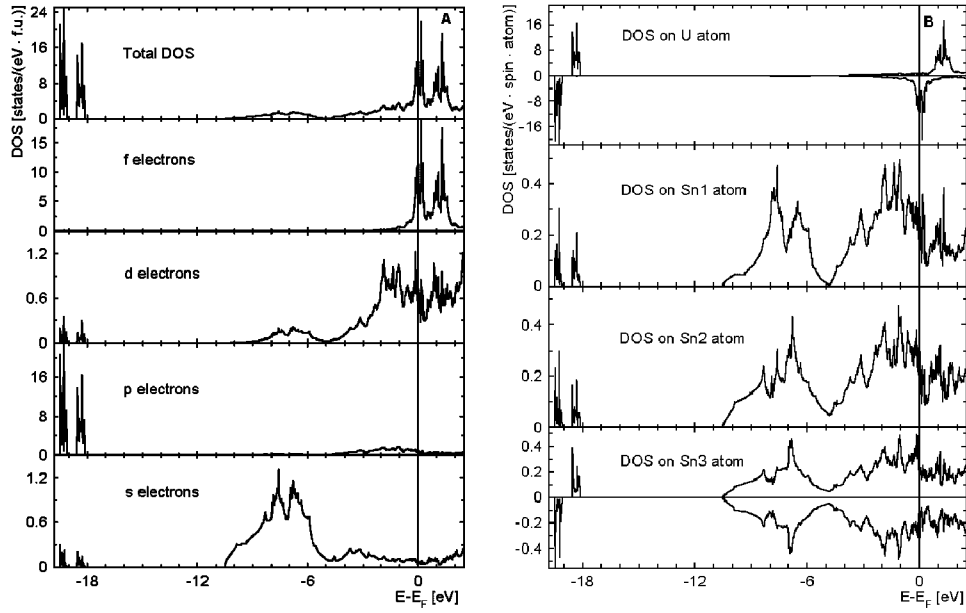


Fig. 2. The DOS plots for USn_2 compound: (A) total and l -decomposed; (B) local (let us note that for U and Sn3 atoms the DOS plots are presented for two spin directions).

the U atoms and surrounding atoms are the following: 3.176 Å, 3.194 Å, 3.178 Å, and 3.858 Å for Sn1, Sn2, Sn3, and U atoms, respectively. The U($6p$) electrons form subbands, which have about 0.4 eV of width. The similar subbands are formed by U($6p$) electrons in UGe_2 compound [22]. In the case when interuranium distances are larger the U($6p$) electrons form very narrow bands (e.g. for UCu_5Sn compound, where U–U distance is about 5 Å [23]). The range between -10.5 eV and -4.8 eV is occupied mainly by s electrons from Sn atoms (see Fig. 3B–D). The DOS located above Sn s electrons up to the Fermi level are composed of Sn(p) and U(d, f) electrons. The U($5f$) electrons provide the main contribution to the total DOS at the Fermi level, about 86% of the value 12.007 states/(eV f.u.). The calculated value of the Sommerfeld coefficient γ_0 in the linear term of the heat capacity is equal to 28.3 mJ/(mol K²). This value is close to the experimental value γ obtained by Dhar et al. [6]: 28 mJ/(mol K²). The theoretical value should be lower than the experimental one because of an enhancement factor λ , $\gamma = (1 + \lambda)\gamma_0$, which has positive value. Uncertainty of γ_0 is magnified because of location of E_F on the slope of sharp DOS peak. The U($5f$) electrons form a relatively wide band occupied by about 3.2 electrons, having the centre of gravity above E_F . The occupation numbers and DOS at the Fermi level for particular atoms are collected in Tables II and III, respectively. The occupation numbers collected in Table II allow calculating the spin magnetic moments. The total magnetic moment is predominantly located on U atoms (2.566 μ_B /U atom). The main contribution

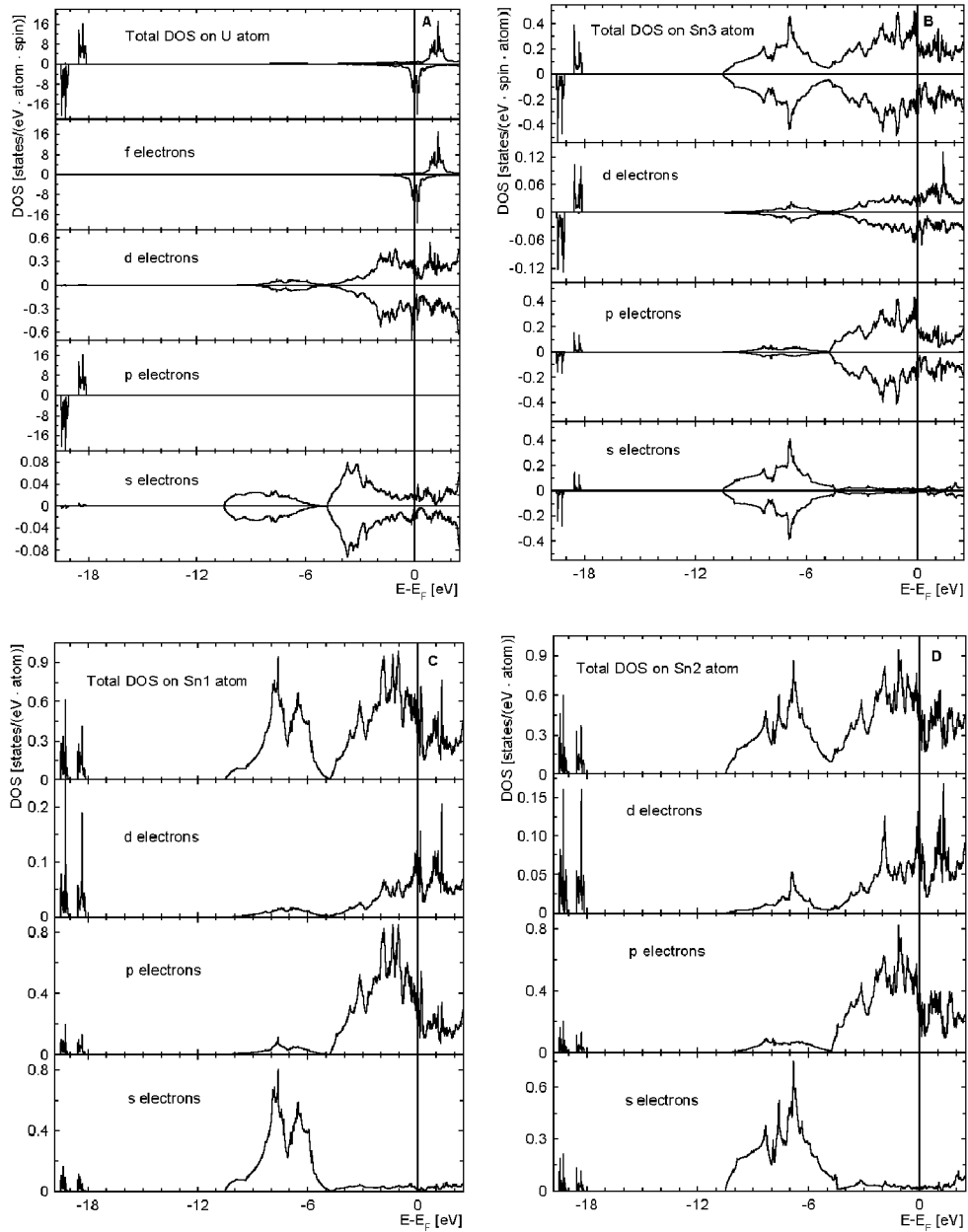


Fig. 3. The local and l -decomposed DOS plots for USn_2 compound: (A) and (B) for U and Sn3 atoms, respectively, presenting results for two spin directions; (C) and (D) for Sn1 and Sn2 atoms, respectively, presenting results for one spin direction (no magnetic moment on these atoms).

TABLE II

Number of states for USn_2 compound (per atom or unit cell and spin).

Atom (site)	Spin	s	p	d	f	Total
U(4j)	↑	0.249	3.037	0.989	0.415	4.690
	↓	0.268	3.041	1.153	2.794	7.256
Sn1(4i)	↑ or ↓	0.785	1.062	0.120	0.046	2.013
Sn2(2a)	↑ or ↓	0.787	1.037	0.151	0.059	2.034
Sn3(2c)	↑	0.784	1.028	0.132	0.051	1.995
	↓	0.778	0.999	0.156	0.061	1.994
Total (per cell)	↑	7.278	20.526	5.000	2.064	34.868
	↓	7.342	20.484	5.706	11.600	45.132

TABLE III

Density of states at the Fermi level for USn_2 compound (per atom or f.u. and spin).

Atom (site)	Spin	s	p	d	f	Total
U(4j)	↑	0.020	0.014	0.238	0.402	0.674
	↓	0.021	0.024	0.288	9.867	10.200
Sn1(4i)	↑ or ↓	0.007	0.197	0.050	0.029	0.283
Sn2(2a)	↑ or ↓	0.009	0.223	0.053	0.053	0.338
Sn3(2c)	↑	0.011	0.155	0.035	0.009	0.210
	↓	0.003	0.157	0.037	0.051	0.248
Total (per f.u.)	↑	0.037	0.400	0.332	0.462	1.231
	↓	0.034	0.411	0.383	9.948	10.776

is provided by U($5f$) and U($6d$) electrons (2.379 and 0.164 μ_B /U atom, respectively). The magnetic moments in the unit cell presented in Fig. 1 are parallel. The antiferromagnetic situation is obtained expanding the cell along c axis. A very small moment, antiparallel to the uranium one, is induced on Sn3 atom, $\approx 0.001 \mu_B$ /Sn3 atom. The resultant moment is an effect of opposite polarization of particular types of electrons. The contributions to the Sn3 total magnetic moment are the following: 0.006, 0.029, -0.026 , and $-0.010 \mu_B$ for s , p , d , and f electrons, respectively. Comparing calculated spin magnetic moment of the U atom and the resultant experimental value 1.56 μ_B /U atom [7] one can estimate orbital moment located on uranium atoms. The orbital moments on U atoms are antiparallel to the spin ones and their values are equal to about 4 μ_B /U atom. The value is of the order of typical values obtained by fully relativistic codes reported for UGe_2 (2.85–3.18 [16]), UFe_5Al_7 (2.44 [24]), or USb (3.42 [25]).

For U and Sn3 atoms the spin projected DOS plots are presented in Figs. 1B, 2A, and 2B. In the case of Sn3 the differences in the spin projected DOS are visible only in the vicinity of the Fermi level. For Sn1 and Sn2 atoms (Figs. 3C, D) the spin projection is not necessary, the calculated moments are below $10^{-5} \mu_B/\text{Sn}$ atom, value beyond experimental resolution and within computational error.

4. Conclusions

The presented results of spin polarized band structure calculations for USn_2 compound show that the magnetic moments are formed mainly by U(5*f*) and U(6*d*) electrons and order antiferromagnetically. The three types of Sn atoms may be treated as non-magnetic. The magnetic unit cell is composed of the crystallographic cell doubled along *c* axis.

Acknowledgment

Work supported by the State Committee for Scientific Research grant No. 2 P03B 023 22 and the Centre of Excellence for Magnetic and Molecular Materials for Future Electronics within the European Commission contract No. G5MA-CT-2002-04049. The calculations were performed at the Supercomputing and Networking Centre of Poznań (PCSS).

References

- [1] D.A. Treick, J.H. Carter, A.I. Snow, B.R. Baldwin, A.S. Wilson, *The Uranium-Tin System*, US Atomic Energy Comm. M-3107 (1945).
- [2] R.I. Sheldon, E.M. Foltyn, D.E. Peterson, *Bull. Alloy Phase Diagrams* **8**, 347 (1987).
- [3] C. Sari, F. Varenza, W. Muller, *J. Less Common Met.* **92**, 301 (1983).
- [4] A. Palenzona, P. Manfrinetti, *J. Alloys Comp.* **221**, 157 (1995).
- [5] P. Boulet, H. Noël, *Solid State Commun.* **107**, 135 (1998).
- [6] S.K. Dhar, Y. Kimura, M. Kouzaki, K. Sugiyama, R. Settai, Y. Onuki, T. Takeuchi, K. Kindo, P. Manfrinetti, A. Palenzona, *Physica B* **245**, 210 (1998).
- [7] P. Boulet, G. André, F. Bourée, H. Noël, *J. Alloys Comp.* **329**, 47 (2001).
- [8] A. Hasegawa, *J. Magn. Magn. Mater.* **52**, 425 (1985).
- [9] D.D. Koelling, M.R. Norman, A.J. Arko, *J. Magn. Magn. Mater.* **63-64**, 638 (1987).
- [10] M. Olšovec, M. Diviš, *Phys. Status Solidi B* **195**, K13 (1996).
- [11] A.L. Cornelius, A.J. Arko, J.L. Sarrao, J.D. Thompson, M.F. Hundley, C.H. Booth, N. Harrison, P.M. Oppeneer, *Phys. Rev. B* **59**, 14473 (1999).
- [12] A. Szajek, *Phys. Status Solidi B* **236**, 552 (2003).
- [13] A. Szajek, *J. Magn. Magn. Mater.* **272-276**, e347 (2004).

- [14] H. Takahashi, N. Mori, Y. Onuki, S.W. Yun, *Physica B* **186-188**, 772 (1993).
- [15] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheiken, D. Braithwaite, J. Flouquet, *Nature* **406**, 587 (2000).
- [16] A.B. Shick, W.E. Pickett, *Phys. Rev. B* **86**, 300 (2001).
- [17] O.K. Andersen, O. Jepsen, M. Šob, in: *Electronic Structure and Its Applications*, Ed. M.S. Yussouff, Springer, Berlin 1987, p. 2.
- [18] G. Krier, O. Jepsen, A. Burkhardt, O.K. Andersen, *The TB-LMTO-ASA Program*, source code version 4.7, available upon request from the program authors.
- [19] B.I. Min, Y.-R. Jang, *J. Phys., Condens. Matter* **3**, 5131 (1991).
- [20] U. von Barth, L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- [21] P. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* **49**, 16 223 (1994).
- [22] A. Szajek, *Cryst. Res. Technol.* **36**, 1105 (2001).
- [23] G. Chełkowska, J.A. Morkowski, A. Szajek, R. Troć, *J. Phys., Condens. Matter* **14**, 3199 (2002).
- [24] C. Cardoso, L.M. Sandratskii, T. Gasche, M. Godinho, *Phys. Rev. B* **65**, 094413 (2002).
- [25] H. Yamagami, *Phys. Rev. B* **61**, 6246 (2000).