ELECTRONIC STRUCTURE
AND PHOTOEMISSION SPECTRA OF USn₂ COMPOUND

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Abstract: The band structure calculations have been performed for USn_2 compound based on the tight binding linear muffin-tin orbital (TB LMTO) method. The calculations have confirmed the antiferromagnetic order in the USn_2 system, crystallizing in the $ZrGa_2$-type structure with one uranium and three tin crystallographic sites. The magnetic moment is predominantly located on the uranium atoms and is formed mainly by the f electrons. The calculated X-ray photoemission spectra are presented.

1. INTRODUCTION

Wide range of properties of the uranium 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. Systematic studying of binary phase diagrams leads to understanding of nature of such phenomena as Pauli paramagnetism, spin fluctuations, heavy fermions, magnetic ordering or superconductivity. Different types of the uranium environments lead to such unique phenomena and influence on electronic structure of the considered compounds. The U-Sn phase diagram is composed of seven phases [1, 2]: USn_3 ($AuCu_3$ type), U_3Sn_7 (Ce_3Sn_7 type), USn_2 ($ZrGa_2$ type), USn (ThIn type) and U_5Sn_4 (Ti_5Ga_4 type). Growing concentration of the tin atoms in these compounds leads to different magnetic ordering [2-4]: from ferromagnetic for USn and U_5Sn_4, through antiferromagnetic for U_3Sn_7 and USn_2, to nonmagnetic spin fluctuating system USn_3. 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 $U(5f)$ electrons with those of the ligands (Sn, Ge).

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. Till now, for binary U-Sn systems, the band structure calculations were reported for two compounds: USn_3 [5-8] and USn [9].

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 [10]. Saxena et al. [11] have found that around 1 GPa UGe_2 becomes superconducting while remaining ferromagnetic ($m \approx \mu$ /U atom) providing a novel example of coexistence of the superconductivity and ferromagnetism.

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) [12, 13]. For computations, the neutron diffraction [4] experimental values of the lattice parameters were assumed. In the crystal structure of USn_2 uranium atoms occupy one position U($4j$) and tin atoms occupy three crystallographic positions marked as Sn1($4i$), Sn2($2a$) and Sn3($2c$) sites. The unit cell accommodates four formula units.

The starting atomic configurations were assumed as core $+6p^6 5f^3 6d^1 7s^2$ for U, and core $+5s^2 5p^2$ 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 [12] 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 [14] was adopted. The von Barth-Hedin [15] 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 [16]. The computed partial densities of states (DOS) for the constituent atoms in the compound multiplied by the respective weight factors proportional to the atomic cross-sections for photon scattering (provided in Ref. [17]) and convoluted with the Gaussian function gave the calculated X-ray photoemission spectra. The parameter for the Gaussian distribution was taken equal to the assumed experimental resolution $\delta = 0.3$ eV.

3. RESULTS AND DISCUSSION

The *ab-initio* calculations were performed with and without spin polarization. The first procedure was used for magnetic unit cell, which is composed of double crystallographic cell expanded along c axis, as it was suggested by neutron diffraction (see Fig. 3 in Ref. [4]). The second one for photoemission calculations. The densities of states (DOS) are presented in Fig. 1: left panel – paramagnetic state and right panel – antiferromagnetic one. The total DOS for particular panels are decomposed into site projected DOS's and a few characteristic features can be observed. The subbands in the lowest part, about 17.9 eV below the Fermi level ($E_F = 0$) is due to the U($6p$) electrons with small contributions of s and p electrons from Sn atoms, surrounding U atoms as nearest neighbours. The range between -11 and -5 eV is occupied mainly by s electrons from Sn atoms, the DOS above this area up to the Fermi level is composed of Sn(p) and U(d, f) electrons. The main contribution to the total DOS at the Fermi level is provided by U($5f$) electrons: about 86% of the values 12.007 and 7.138 states/(eV $f.u.$) for antiferro- and paramagnetic state, respectively. The site projected DOS and l-decomposed values of DOS at the Fermi level are collected in Table I. Table II contains occupation numbers, which for antiferromagnetic state allow calculating of spin magnetic moments on particular atoms. The total magnetic moment is predominantly located on U atoms. The main contribution to the uranium moment (2.566 μ_B/U atom) is provided by U($5f$) and U($6d$) electrons (2.379 and 0.164 μ_B/U atom, respectively). The calculated value of the total magnetic moment is larger than

Table I. Density of states at the Fermi level for USn$_2$ compound (per atom or f.u. and spin): AFM and PM mean results for antiferro- and paramagnetic state, respectively

Atom (site)	spin	s	p	d	f	Total
U(4j)	AFM ↑	0.020	0.014	0.238	0.402	0.674
	AFM ↓	0.021	0.024	0.288	9.867	10.200
	PM (↑ or ↓)	0.037	0.020	0.492	6.242	6.791
Sn1(4i)	AFM (↑ or ↓)	0.007	0.197	0.050	0.029	0.283
	PM (↑ or ↓)	0.004	0.108	0.034	0.017	0.163
Sn2(2a)	AFM (↑ or ↓)	0.009	0.223	0.053	0.053	0.338
	PM (↑ or ↓)	0.005	0.126	0.024	0.017	0.172
Sn3(2c)	AFM ↑	0.011	0.155	0.035	0.009	0.210
	AFM ↓	0.003	0.157	0.037	0.051	0.248
	PM (↑ or ↓)	0.008	0.156	0.019	0.011	0.194
Total (per f.u.)	AFM ↑	0.037	0.400	0.332	0.462	1.231
	AFM ↓	0.034	0.411	0.383	9.948	10.776
	PM (↑ or ↓)	0.048	0.269	0.548	6.273	7.138

the one obtained from the neutron diffraction experiment (1.56(6) μ_B/U atom [4]) because the orbital moment is not taken into account in the calculations. According to the Hund's rule the spin and orbital moments have antiparallel orientation and the resultant moment has smaller value than the spin one. The Sn atoms can be treated as nonmagnetic: m_{Sn3} = 0.001 μ_B/atom, and moments for Sn1 and Sn2 atoms are less than $10^{-5}\mu_B$/atom.

Table II. Number of states for USn$_2$ compound (per atom or unit cell and spin): AFM and PM mean results for antiferro- and paramagnetic state, respectively

| Atom (site)	spin	s	p	d	f	Total
U(4j)	AFM ↑	0.249	3.037	0.989	0.415	4.690
	AFM ↓	0.268	3.041	1.153	2.794	7.256
	PM (↑ or ↓)	0.268	3.066	1.114	1.575	6.023
Sn1(4i)	AFM (↑ or ↓)	0.785	1.062	0.120	0.046	2.013
	PM (↑ or ↓)	0.796	1.104	0.062	0.023	1.985
Sn2(2a)	AFM (↑ or ↓)	0.787	1.037	0.151	0.059	2.034
	PM (↑ or ↓)	0.804	1.099	0.078	0.030	2.011
Sn3(2c)	AFM ↑	0.784	1.028	0.132	0.051	1.995
	AFM ↓	0.778	0.999	0.156	0.061	1.994
	PM (↑ or ↓)	0.800	1.069	0.075	0.029	1.973
Total (per cell)	AFM ↑	7.278	20.526	5.000	2.064	34.868
	AFM ↓	7.342	20.484	5.706	11.600	45.132
	PM (↑ +↓)	14.928	42.032	10.020	13.020	80.000

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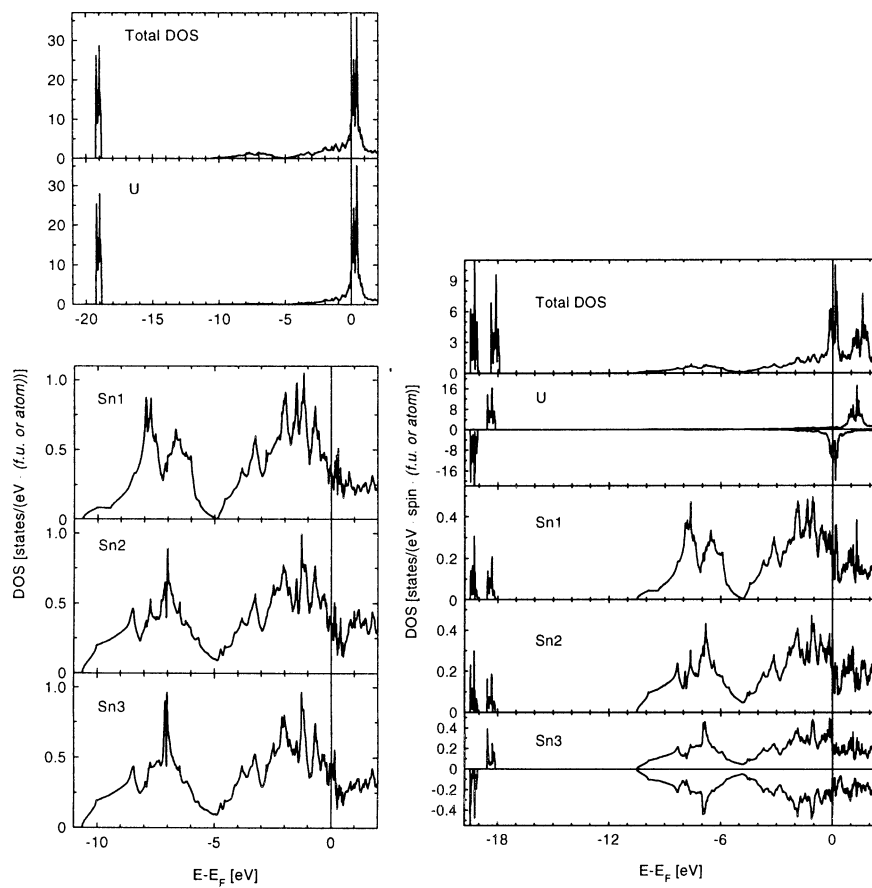
Fig. 1. The DOS plots for USn$_2$ compound in para- (left panel) and antiferromagnetic (right panel) state: total (per f.u.) and local (per atom)
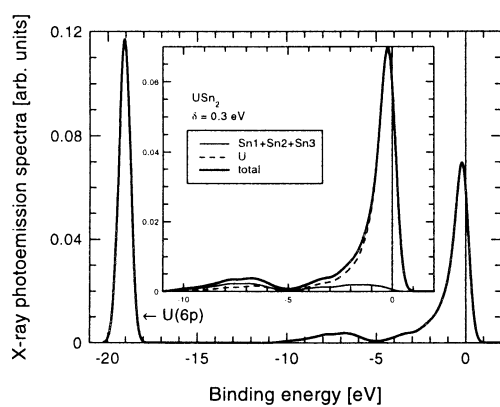

Fig. 2. The calculated XPS spectrum for USn$_2$ compound

The calculations performed for ferromagnetic alignment of magnetic moments gave the total energy higher than for the antiferromagnetic case.

Figure 2 presents calculated photomission spectra, total and decomposed into U and Sn contributions. The spectrum in the vicinity of the Fermi level is dominated by the uranium electrons ($5f$) because of their large values of DOS and larger cross section than for Sn electrons.

4. CONCLUSIONS

The presented results of *ab-initio* spin polarized band structure calculations for USn_2 compound show that the magnetic moments order antiferromagnetically and are formed mainly by $U(5f)$ and $U(6d)$ electrons. The Sn atoms may be treated as nonmagnetic. The magnetic unit cell is composed of the crystallographic cell doubled along c axis what is consistent with neutron diffraction data. The photoemission spectrum is dominated by the uranium contribution.

Acknowledgement

References

[1]   A. Palenzona and P. Manfrinetti, J. Alloys Compd. **221**, 157 (1995).
[2]   P. Boulet and H. Noël, Solid State Commun. **107**, 135 (1998).
[3]   S. K.Dhar, Y. Kimura, M. Kouzaki, K. Sugiyama, R. Settai, Y. Onuki, T. Takeuchi, K. Kindo, P. Manfrinetti, A. Palenzona, Physica **B245**, 210 (1998).
[4]   P. Boulet, G. Andreé, F. Bourée, H. Noël, J. Alloys Compd. **329**, 47 (2001).
[5]   A. Hasegawa, J. Magn. Magn. Mat. **52**, 425 (1985).
[6]   D. D. Koelling, M. R. Norman, A. J., Arko, J. Magn. Magn. Mat. **63-64**, 638 (1987).
[7]   M. Olšovec, M. Diviš, phys. stat. sol. (b) **195**, K13 (1996).
[8]   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. **B59**, 14473 (1999).
[9]   A. Szajek, phys. stat. sol. (b) **236**, 552 (2003).
[10]   H. Takahashi, N. Mori, Y. Onuki, S. W. Yun, Physica **B186-188**, 772 (1993).
[11]   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).
[12]   O. K. Andersen, O. Jepsen, M. Šob, in *Electronic Structure and Its Applications*, edited by M. S. Yussouff (Springer, Berlin, 1987), p. 2.
[13]   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).
[14]   B. I. Min, Y.-R. Jang, J. Phys.: Condens. Matter **3**, 5131 (1991).
[15]   U. von Barth, L. Hedin, J. Phys. **C5** 1629 (1972).
[16]   P. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. **B49**, 16223 (1994).
[17]   J. J. Yeh, I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).