Electronic property of ThSn$_3$ in comparison with uranium and transuranium compounds

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Abstract. Energy band structures of AnSn$_3$ (An=Th, U, Np, and Pu) are investigated by a relativistic linear augmented-plane-wave method with the exchange-correlation potential in a local density approximation. It is found in common that the energy bands in the vicinity of the Fermi level are mainly due to the hybridization between actinides 5$f$ and Sn 5$p$ electrons. The similarity is basically understood by the change of electron numbers inside the Fermi surfaces on the basis of a rigid-band picture.

1. Introduction
Actinide AnSn$_3$ compounds with the AuCu$_3$-type cubic crystal structure, where An means an element belonging to the actinide group (Th, U, Np, and Pu) of the periodic table, show an interesting trend of 5$f$-electron characters. ThSn$_3$ and PuSn$_3$ are Pauli paramagnets, USn$_3$ is a spin-fluctuating compound, and NpSn$_3$ is an antiferromagnet with the Néel temperature of 9.5K[1]. This trend is closely related to the lattice constant (ThSn$_3$: 4.719 Å, USn$_3$: 4.626Å, NpSn$_3$: 4.627Å and PuSn$_3$: 4.630Å)[1, 2, 3]. The corresponding electronic specific heat coefficient $\gamma$ increases with increasing the lattice constant (USn$_3$: 170 and NpSn$_3$: 88 mJ/K$^2$-mol)[1, 4].

In this paper, we try to understand what the key issues are to construct the energy band structures around the Fermi energy for ThSn$_3$, USn$_3$, NpSn$_3$, and PuSn$_3$, we attempt to unveil 5$f$ electron properties purely originating from actinide atoms.

2. Method of Band Calculation
The calculations for the energy band structures are carried out by using the relativistic linear augmented-plane-wave (RLAPW) method. All 5$f$ electrons are assumed to be itinerant and the calculations are performed in the paramagnetic phase. Note here that relativity should be taken into account, because of large atomic numbers of the constituent atoms. The spatial shape of the one-electron potential is determined in the muffin-tin approximation, and we use the exchange and correlation potential in the local density approximation (LDA). The self-consistent calculation is carried out for the experimental lattice constant.

AnSn$_3$ (An=Th, U, Np, and Pu) materials are categorized into the AuCu$_3$-type structure, which is characterized by the space group Pm3m. The 5$f$ electrons in AnSn$_3$ (An=U, Np, and Pu) are assumed to be itinerant. The iteration process for solving the Dirac one-electron equation starts with the crystal charge density that is constructed by superposing the relativistic atomic
charge densities for neutral atoms Th([Rn]5f^66d^17s^2), U([Rn]5f^66d^17s^2), Np([Rn]5f^46d^17s^2), Pu([Rn]5f^56d^17s^2), and Sn([Kr]4d^{10}5p^25s^2), where [Rn] and [Kr] symbolically indicate the closed electronic configuration for radon and krypton, respectively. In the relativistic atomic calculation, the spin-orbit splitting in Th 5f, U 5f, Np 5f, Pu 5f, and Sn 5p states are found to be 30 mRyd., 60 mRyd., 70 mRyd., 80 mRyd., and 29 mRyd., respectively. Note here that mRyd. denotes milli-Rydberg and 1 Ryd.=13.6 eV.

3. Results of Band Calculation
First let us discuss the calculated results for ThSn₃ and PuSn₃ as shown in Figure 1(a) and (b), in which we depict the energy band structure along the symmetry axes in the Brillouin zone in the energy region from 0.3 Ryd. to 1.0 Ryd.. Note here that the three Th(Pu) 6p and fifteen Sn 4d bands in the energy range between −1.5 Ryd. and −0.6 Ryd. are not shown in Figure 1, since those bands are irrelevant to the present discussion.

The Fermi levels are found to be 0.536 Ryd., 0.563 Ryd., 0.547 Ryd., and 0.551 Ryd. for ThSn₃, USn₃, NpSn₃, and PuSn₃, respectively. The overall change in the 5f bands among AnSn₃(An=Th, U, Np, and Pu) is characterized by a downward shift of the Fermi level, but in any case, the present calculations performed in the paramagnetic phase conclude that NpSn₃ is metal, while in actuality, there is antiferromagnet. These points should be improved in future by applying the modified method which includes effectively a spin-polarized interactions. Concerning the energy band structure in the vicinity of $E_F$, we emphasize that there always occurs a hybridization between actinide 5f and Sn 5p states among four materials. Above $E_F$ near R point, the flat 5f bands split into two groups, corresponding to the total angular momentum $j=5/2$ (lower bands) and 7/2 (upper bands).

The calculated total density of states (DOS) for (a) USn₃ and (b) NpSn₃ are shown in Figure 2. The 5f bands are split into two subbands by the spin-orbit interaction and due to the hybridization between 5f and 5p electrons, finite DOS always appear at the Fermi
Figure 2. Density of states for (a) USn$_3$ and (b) NpSn$_3$. Solid curves show the total density of states. Dashed line indicates the Fermi energy.

level. The total density of states at $E_F$ are evaluated as $D(E_F) = 42.8$ states/Ryd.cell, 97.7 states/Ryd.cell, 150.3 states/Ryd.cell, and 31.4 states/Ryd.cell in the ThSn$_3$, USn$_3$, NpSn$_3$, and PuSn$_3$, respectively. By using these values, the theoretical specific heat coefficient $\gamma_{\text{band}}$ are 7.4, 16.9, 26.0, and 5.4 mJ/K$^2$-mol for ThSn$_3$, USn$_3$, NpSn$_3$, and PuSn$_3$, respectively.

It is easily recognized in Figure 1(a) that for ThSn$_3$ there exist two small hole sheets and one electron sheet of the Fermi surface in the 7th, 8th and 9th bands, respectively. Because of the energy dispersion relation around the $\Gamma$ point, it is natural to consider the large Fermi surface in the 9th band as the large electron sheet, which is shown with the simple cubic Brillouin zone in Figure 3(a). The 9th band has two kinds of sheets. One is a set of there equivalent small electron pockets, each of which is centered at the M point. Another sheet in the 9th band is a large electron sheet which is centered at the $\Gamma$ point. The shape of the large electron sheet is essentially spherical but deeply concave in $\langle 111 \rangle$ directions. It has a small hollow at the center, and eight concavities are connected with each other via the small hollow. The shape of ThSn$_3$ these sheets are similar to the Fermi surface for CeSn$_3$[6].

The energy band structure for USn$_3$ is quite similar to that for UGe$_3$[7, 8]. The dispersion of the 5$f$ bands in the vicinity of the R point is still appreciably large. The Fermi surface consists also of the two hole sheets in the 8th and the 9th bands and an electron sheet in the 10th band. The Fermi surfaces in the 9th and 10th bands are shown in Figure 3(b) and (c), respectively.

Figure 3. (a) The electron-Fermi surface in the 9th band for ThSn$_3$ centered at the $\Gamma$ point. (b) The hole- and (c) electron-Fermi surfaces in the 9th band and 10th band for USn$_3$ centered at the R point, respectively.
Figure 4. (a) The electron- and (b) hole-Fermi surfaces in the 9th band for NpSn$_3$ centered at the R and the $\Gamma$ point, respectively. (c) The electron-Fermi surfaces in 11th band for PuSn$_3$ centered at the R point.

The Fermi surface in the 10th band looks like a soccer ball and is composed of a large hollow electron sheet centered at the R point and thin cushion-like electron pockets split from a main part, centered at each M points as shown in Figure 3(c).

Figure 4 shows (a) the electron and (b) hole sheets in the 9th band for NpSn$_3$. The electron sheet centered at the R point is similar to the hole Fermi surface in the paramagnetic state in NpIn$_3$ reported by D. Aoki et al.[1]. We suppose that some open orbits might be existed on this Fermi surface.

The Fermi surfaces in PuSn$_3$ are composed of a hole sheet and two kinds of electron sheets. The 10th band has a hole sheet centered at the $\Gamma$ point and this shape is cube-like. The 11th band has three dumbbell-like electron sheets lying on each $\Delta$ axis and three starfish-like electron sheets centered at each M point which is shown in Figure 4(c).

4. Discussion and Conclusion
We have applied the RLAPW method to the self-consistent calculation of the electronic structure for ThSn$_3$, USn$_3$, USn$_3$, and PuSn$_3$ on the basis of the itinerant 5$f$ electron picture by assuming the non-magnetic phase. We found that a hybridization between the 5$f$ and Sn 5$p$ states occurs in the vicinity of $E_F$. The similarity in the Fermi surface structure among AnSn$_3$ compounds has been found to be understood based on the rigid-band picture. The different nature of 5$f$ orbital may be a key issue to understand the magnetism of AnSn$_3$ compounds.

Theoretical de Haas-van Alphen frequencies and the cyclotron effective mass for each frequency branches which originate from AnSn$_3$ will be calculated and published elsewhere.

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