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AN ANALYSIS OF THE SERIES OF MODERATELY HEAVY FERMION MATERIALS: $CeSn_3$, USn_3, AND $NpSn_3$*

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The materials $CeSn_3$, USn_3, and $NpSn_3$ are all moderately heavy Fermion compounds with electronic specific heat coefficients of 73, 169, and 242 mJ/mole K^2. $CeSn_3$ is known as a mixed valent system and $NpSn_3$ is a weak itinerant antiferromagnet. All three are strongly enhanced. Being in the relatively simple Au_3Cu structure, they form an excellent set of materials to study as representatives of strongly enhanced systems. One would like to ascertain what properties can be determined from band calculations based on density functional theory in the local density approximation. It has already been shown that the Fermi surface topology of $CeSn_3$ can be well described in this way even though the experimental masses are much larger than the band results. The enhancement factor for USn_3 is even larger and $NpSn_3$ is indeed predicted to go magnetic. We present here fully relativistic SCF calculations for these materials and discuss the relation between our results and what is known experimentally.

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The classic signature of a heavy Fermion system is an enormous electronic specific heat. This would imply both a large density of states (DOS) at the Fermi energy (E_F) and strong enhancement effects. To date, all such systems are f-electron materials with their exotic properties attributed to the nearly local behavior of the f orbitals. One can easily make the case that this phenomenon is the boundary region between itinerant and localized f electrons. Given the large DOS (even accounting for large enhancements), it is natural to wonder why these materials do not relax by crystallographic transformation, magnetic transition, or superconducting transition. Clearly, this does happen more often than not as $CeCu_2Si_2$, UPt_3, and UBe_{13} become superconducting and U_2Zn_{17}, UCd_{11}, and $CePb_3$ go magnetic. Probably the best tool to sort out the issues of this boundary region is the establishment of the systematics with the variation of the f atom element or the ligand. As has been pointed out, the Au_3Cu structured materials offer a particularly advantagous set within a common crystal structure which freezes one important parameter of the problem. The UX_3 materials provide a very useful, complete sequence as one goes from the very itinerant USi_3 to the local moment antiferromagnetic UPb_3 [1]. USn_3 [2] exhibits a very large electronic specific heat coefficient (169 mJ/mole K^2), yet does not undergo a transition. Replacing 8% of the Sn by Pb, though, will drive the compound antiferromagnetic [3]. The tin system is obviously near the boundary region and it is important to seek other variations. This is provided by mixed valent $CeSn_3$ (73 mJ/mole K^2 [4]) and $NpSn_3$ which undergoes a transition to an antiferromagnetic phase [5]. $NpSn_3$ exhibits an electronic specific heat of 242 mJ/mole K^2 above the transition and 88 mJ/mole K^2 below. A comparison of these materials offers a different view of the transition than through ligand variation. In this case, one is varying the number of f electrons on the f atom site so more of the f bands are being pulled down to the Fermi level. An important question to ask is how well do band structure calculations within the local density approximation work in describing the ground state properties of these materials. The reason the above series was chosen was that extensive work had already been done on $CeSn_3$. de Haas-van Alphen (dHvA) measurements on this compound revealed delocalized f electrons at the Fermi energy [6]. Moreover, the experimental Fermi surface topology agreed rather well with the topology predicted by band calculations [7]. The experimental masses, though, were substantially higher than the theoretical masses in line with the large underestimation of the electronic specific heat coefficient by the band calculations. This was not suprising since the masses are an excited state property and not a ground-state one. With the above success with $CeSn_3$, it is natural to similarly analyze USn_3 and $NpSn_3$.

The band structure method employed was the standard LAPW method [8]. Results reported here use either an exchange-only local potential ($\alpha = 2/3$) or exchange plus von Barth-Hedin (vBH) correlation [9]. The question of relativistic effects are important for these compounds and thus merits some disussion. For $CeSn_3$ and USn_3, full relativistic calculations within a quaternian formalism were performed [10]. An exchange-only potential was used for $CeSn_3$ to facilitate comparisons to the previous scalar relativistic calculation [7] (that calculation included spin-orbit coupling as a perturbative step at the end of the self-consistency cycle), and a vBH potential was used for USn_3 and $NpSn_3$. For $NpSn_3$, spin-orbit coupling was treated as a second variational step using the scalar relativistic eigenvectors as input. This step, though, was done within the self-consistency cycle. The advantages of this are two-fold: (i) computational time is reduced by about a factor of five over the full relativistic case and (ii) moment polarization effects can also be included in the second variational step. The latter will be necessary to describe the antiferromagnetic phase of $NpSn_3$ (this calculation is being set up but has not yet been performed). As a test, the output potentials for $NpSn_3$ were used as input to the full relativistic code and a single iteration was done. Very few changes occured, indicating that the above approximation is sound for these compounds.

In Table 1, the DOS at E_F are shown for the various calculations. Treating spin-orbit as a perturbation worked very well for $CeSn_3$ but not for U and $NpSn_3$. The effect of correlation is weak and leads to a slight increase in the DOS as the f's are energetically lowered. The enhancement factors, equal to exp./theory - 1, are large and of similar size for $CeSn_3$ and USn_3. For $NpSn_3$, the calculated DOS is enormous resulting in a smaller enhancement factor. This occurs because the Fermi energy is tied to a very sharp peak about 40 K wide with height about 135 mJ. The accuracy of the calculation for such a sharp structure may be questioned. We used a Fourier series spline fit of 331 star functions to bands found at 120 K vectors in the irreducible wedge of the simple cubic zone to calculate the DOS from a linear tetrahedron method with 4096 tetrahedra in the wedge. Also note that the 242 mJ experimental number is determined somewhat above the transition temperature (9.5 K) and temperature broadening effects will be significant for such a high DOS.

The value of the Stoner interaction factor, I, that will make the susceptibility diverge is also given in the table along with the local spin density (LDS) estimates of the actual value of I. It is seen that

$CeSn_3$ is predicted to be paramagnetic, USn_3 is on the borderline, and $NpSn_3$ is definitely predicted to be magnetic.

The band structures for these compounds are similar with three bands (8, 9, and 10) being relatively dispersionless and degenerate over a large part of the Brillouin zone. The flat part of these bands are about 25 mRy above E_F in $CeSn_3$, about 8 mRy above in USn_3, and at E_F for $NpSn_3$. This is what is responsible for the increase in the DOS. Spin-orbit effects are crucial for U and Np. A scalar relativistic calculation for $NpSn_3$ places the flat part of these bands about 3 mRy above E_F. The inclusion of spin-orbit as a perturbation causes the bands to fall below E_F by 6 mRy, whereas a self-consistent treatment of spin-orbit terms places this structure at E_F.

The Fermi surfaces for USn_3 and $NpSn_3$ are similar with hole pockets around R for bands 8 and 9 and a complicated electron surface for band 10. Unlike $CeSn_3$, no Γ-centered pieces are found. In Table II, some representative Fermi surface orbital areas and masses are shown. These are shown for surfaces around the R point at which the three f bands are virtually degenerate. One sees a general decrease in the orbital areas and an increase in the masses as one moves from Ce to U to Np. Some of the band masses were so high for band 10 in $NpSn_3$ that the orbits could not be traced. But for USn_3, some of the band masses for band 10 are low enough (<1), that even with a mass enhancement factor, the orbits should be seen in dHvA experiments if adequate samples become available.

The major part of the mass enhancements can be attributed to paramagnons. From a density functional view point, this can be understood as follows. The calculation performed is for a paramagnetic ground state. The electrons, though, are unstable to low energy polarized excitations. These are described by the spin-spin part of the response function. In particular, the self-energy looks like [11]

$$\sum \alpha \int G \frac{I}{I - I\chi} \qquad (1)$$

where G is the non-interacting Green's function, I is the interaction factor, and χ the generalized susceptibility. The integral is to be performed over all wave vectors and frequencies. The resulting mass enhancement over the band mass is (energy is in Rydbergs)

$$\frac{m^*}{m_{\text{band}}} = \left(1 - \frac{\partial\sum}{\partial\omega}\right)\Big/\left(1 + \frac{1}{2k_F}\,\frac{\partial\sum}{\partial p}\right) \qquad (2)$$

evaluated on the Fermi surface with ω as the frequency and p the wave vector. The above equations are very formidable (they have not been solved for any realistic solid to the authors' knowledge), but one can see that a large Stoner enhancement should lead to a large mass enhancement.

In conclusion, these preliminary results indicate that the band calculations will be useful in ascertaining the properties of enhanced compounds. The large anisotropy of the Fermi surface (note there was not even any Γ centered pieces for USn_3 and $NpSn_3$) casts doubts on models which employ simple spherical Fermi surfaces to describe enhanced compounds. Also interesting was the prediction of near instability in USn_3 and magnetic order for $NpSn_3$. As $NpSn_3$ is an itinerant antiferromagnet with a small moment, we are most anxious to complete the moment polarized calculation to see how the system changes. More experimental work, especially dHvA work, should be attempted on these systems in order to further substantiate the validity of the local density calculations.

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Table I. DOS at E_F for Ce, U, and $NpSn_3$ compared to the experimental electronic specific heats in units of mJ/mole K^2. The third column is the enhancement factor (exp./band - 1). The fourth column gives the value of I that will make the susceptibility diverge with the LSD estimates for I given in the last column. XO is exchange-only, vBH is von Barth-Hedin correlation, SR is scalar relativistic with perturbative spin-orbit, FR is full relativistic, and R is scalar relativistic with self-consistent spin-orbit.

	Band	Exp.	λ	I_{div}	I_{LSD}
$CeSn_3$ (SR) (XO)	12.3	73	4.9	14.1	8.9
$CeSn_3$ (SR) (vBH)	13.2	73	4.5	13.1	9.5
$CeSn_3$ (FR) (vBH)	12.5	73	4.8	13.9	
USn_3 (FR) (vBH)	22.6	169	6.5	7.7	11.6
$NpSn_3$ (R) (vBH)	101.3	242	1.4	1.7	14.5 (SR)

Table II. Orbital areas and masses for Ce, U, and $NpSn_3$. Units are megaGauss for the areas and electron masses for the masses.

		$CeSn_3$	USn_3	$NpSn_3$
Band 8	Area	79.61	39.65	4.50
R center	Mass	0.75	3.93	1.98
H=<111>				
Band 9	Area		57.07	3.22
R center	Mass		5.22	2.69
H=<111>				
Band 10	Area			9.59
R center	Mass			10.37
H=<001>				