Influence of unoccupied 5*f*-band states on the Fermi surface of Th metal*

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The influence of unoccupied 5*f*-band states on the Fermi surface of Th metal is determined by means of highly precise calculations of the Fermi-surface areas and effective masses. Comparison with experiment shows excellent agreement when the 5*f* electrons are treated as itinerant, unlike the predictions of the localized (*f* states removed) model. This result adds strong evidence for the itinerant nature of the occupied 5*f* states in the light actinides.

I. INTRODUCTION

Information about the nature (itinerant versus localized) of the 5*f* electrons is important for understanding the properties of the actinide metals. Recent theoretical work[1-3] has shown that, in the light actinide metals (Th-Pu), the 5*f* electrons are sufficiently delocalized in space to significantly overlap their neighboring atoms and to hybridize strongly with the 6*d*- and 7*s*-like bands. These 5*f* states have small Coulomb correlation energy relative to the large effective bandwidth and hence must be considered as itinerant; i.e., they are to be included in and described by energy-band calculations. Their description is in contrast to the case of localized electrons such as the 4*f*'s in the rare earths[4] or the 5*f*'s in the heavier actinides (Am and beyond) where the Coulomb correlation energy is much larger than their effective bandwidths.[3]

Unfortunately, very few experimental tests of this picture have been made on the actinide metals because of the structural complexity at low temperatures making both the interpretation of experimental data and the calculation of their band structures extremely difficult. (This structural complexity itself may be taken as evidence for the spatial extent of the 5*f* orbitals.) The one exception appears to be thorium metal: it is face-centered cubic at low temperature; has no occupied 5*f* states; and since it is obtainable as high-purity single crystals, accurate de Haas–van Alphen (dHvA) measurements[5,6] have been made yielding precise information about its Fermi surface. Since Th was expected not to contain any 5*f* electrons, Gupta and Loucks[7] artifically removed the 5*f* bands from their relativistic augmented-plane-wave (RAPW) calculations, which allowed them to overcome the difficulties found by Keeton and Loucks[8] in their full Slater exchange ($\alpha = 1$) calculations and allowed them, in this pioneering work, to obtain reasonable agreement with the dHvA measurements. Removing *f* states from the calculations of energy bands in the case of rare-earth metals is a procedure associated with what may be considered as the localized model. By contrast, as mentioned above, Koelling and Freeman[3,10] found that the 5*f* states are itinerant and hence must be retained in any band description.

Recently, normal-incidence reflectivity measurements[9] between 0.5 and 6.0 eV have been performed on Th metal giving information about both occupied and unoccupied states in this range about the Fermi energy. These measurements were undertaken in order to discriminate between the theoretical predictions based on the localized and itinerant (or band) descriptions of the 5*f* states because it was thought that the Fermi-surface properties would not allow such a comparison to be made. It was found[9] that the theoretical calculations[3,10] which included the 5*f* states (itinerant model) correctly predict the existence of band-like *f* states 1–5 eV above the Fermi energy.

Because of the importance of this result as providing strong evidence for the prediction that the *occupied* 5*f* states in the lighter actinide metals are itinerant, a highly precise determination of the Fermi surface (FS) of Th was undertaken as a more severe test of the itinerant model. The results of this work, reported here, show a somewhat surprising feature to have emerged: the experimental Fermi-surface dimensions are only consistent with the calculations in which the *f* resonance is included. Furthermore, the detailed study of the Fermi-surface dimensions obtained with the itinerant (*f* state included) model shows them to be in excellent agreement with experiment, unlike the results obtained with the localized-model results. We therefore conclude that, since there is no reason to expect an abrupt change in the nature of these states as they are occupied, this agreement is strong evidence for the itinerant na-

TABLE I. Comparison of the different band results for Th metal. Eigenvalues (given in mRy) are for the underlying transition-metal band structure (d and s-p bands only).

Calculation		A	B	C	D
		d^2s^2 ($\alpha=1$) (f's removed)	d^2s^2 ($\alpha=\frac{2}{3}$) (f's removed)	($\alpha=\frac{2}{3}$) (with f's)	d^3s^1 ($\alpha=\frac{2}{3}$) (with f's)
Γ	6^+	0	0	0	0
	8^+	448	444	443	450
	7^+	...	472	472	478
	8^+	...	697	697	704
L	6^+	161	142	142	144
	4^+	416	412	412	417
	6^+	447	441	442	431
	6^-	...	595	...	...
	6^+	...	894	894	903
	4^+	...	917	917	926
X	6^+	120	122	122	122
	8^+	212	187	187	190
	6^-	702	728	...	...
	7^+	...	905	905	915
	6^+	...	964	964	974
	7^+	...	1005	1005	1015

ture of the occupied 5f states in the lighter actinides.

II. ENERGY-BAND STRUCTURE AND FERMI SURFACE OF fcc THORIUM

The relativistic energy-band structure of fcc Th is now well known to consist of s- and d-like states, as in any high atomic number fcc transition metal.[7–10] For the itinerant model[3,10] (f states included) there are, in addition, f bands located in the range 1–5 eV above E_F. In our investigations,[10] we used different starting potentials in order to examine the dependence of the calculated energy bands on the assumed configuration (occupation number). For example, in comparing the results obtained for the $6d^27s^2$ and $5f^16d^17s^2$ potentials we found a strong similarity between their band structures. In addition, the f states shift by only about 0.05 Ry when going from the d^2s^2 to the $f^1d^1s^2$ configuration. (This is far from the large occupation number sensitivity observed in the rare earths.[4]) In both calculations, the f states lie considerably above the Fermi energy (which is between 0.55 and 0.6 Ry) and is a direct consequence of the choice of the reduced exchange, $\alpha=\frac{2}{3}$ which we used rather than the $\alpha=1$ value used earlier.[7,8] At E_F, the effects of the 5f bands are small but, as we shall see later, are not negligible.

The work reported here is based on four different calculations of the relativistic band structure obtained using the relativistic augmented-plane-wave (RAPW) method with potentials constructed from overlapping atomic charge densities: (a) The Gupta-Loucks (GL) calculation (d^2s^2, $\alpha=1$, f states removed); (b) the calculation for the d^2s^2, $\alpha=\frac{2}{3}$ potential with the f states removed; (c) the calculation for the d^2s^2, $\alpha=\frac{2}{3}$ potential with f states included; and (d) the calculation for the d^3s^1, $\alpha=\frac{2}{3}$ potential with f states included. In the localized model calculation (b) (f states removed), the logarithmic derivatives which represent the f states in the itinerant model are replaced by a linear (in energy) curve which gives this ($l=3$) angular momentum component free-electron-like behavior. Our "f-states-removed" calculation differs somewhat from that of Gupta and Loucks[7] who used full Slater exchange ($\alpha=1$) and merely smoothed out the f-state resonance. Whereas the reduced exchange in our calculation broadens the band structure somewhat, our results give energy separations at selected points which agree within 10 mRy of the values tabulated by Gupta and Loucks.

We compare the results of the different calculations in Table I where the eigenvalues of the underlying transition-metal structure (d and s-p bands, but no f bands) at Γ, L, and X are listed in millirydberg units. The close (millirydberg) agreement between the two $\alpha=\frac{2}{3}$, d^2s^2 calculations (with the 5f states included and excluded, respectively) is very striking—but not unexpected since the states listed do not interact with the f states. The small changes obtained with the $\alpha=\frac{2}{3}$, d^3s^1 configuration potential shows the relative insensitivity of these results to changes of potential. (Larger differences are obtained, however, with the $\alpha=1$ potential of Gupta and Loucks[7] for the reasons already discussed.) The results given in Table I emphasize the basic stable transition-metal structure of the non-f conduction bands. The f states are moved up about 15 mRy in the d^3s^1 configuration calculation relative to the d^2s^2 calculation. They are actually pulled well below the Fermi surface when $\alpha=1$ is used, as found by Keeton and Loucks.[8]

In both models the Fermi surface (FS) shown in Fig. 1 consists of three distinct pieces: (i) a hole surface at the center of the Brillouin zone (BZ) shaped like a rounded *cube* called "superegg"; (ii) electron surfaces on symmetry lines ΓK ($\langle 110 \rangle$) shaped like pairs of "lungs"; and (iii) the hole surfaces on the symmetry lines ΓL ($\langle 111 \rangle$) shaped like "dumbbells" with triangular ends. In comparing their model with experiment,[5,6] Gupta and Loucks[7] concluded that their model was "only in qualitative agreement with the experimental results." In many ways, the agreement obtained is rather remarkable but may be understood in terms of the potential insensitivity of the underlying transition-element band structure found in comparing the Fermi surfaces resulting from the four different calculations. To provide a qualitative idea of these Fermi-surface sensitivities to the assumed model, we have compared the Fermi surfaces resulting from the four calculations (a)–(d) listed above. The

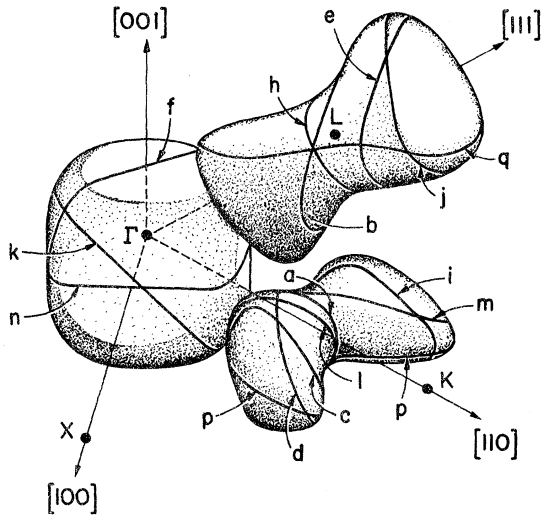

FIG. 1. Gupta-Loucks model Fermi surface for thorium [after Boyle and Gold (Ref. 6)] showing various extremal orbits which are normal to the following symmetry directions: a, c, $[1\bar{1}0]$; b, e, f, [110]; d, [011]; h, j, [111]; i, $[\bar{1}10]$; l, m, [100]; n, p, q, [001]. The orbits p and q were not initially included by Boyle and Gold but have been added by us. The hole cube and the hole dumbbells are centered on the points Γ and L, respectively, while the electron lungs lie across the lines ΓK.

comparison was performed by fitting the eigenvalues obtained for these four calculations with a series of symmetrized plane waves[11] and then making computer printer plots of the Fermi in planes separated by $\pi/10a$. Although we were limited to eighty-seven inequivalent points for the GL data, we were able to obtain fits with an rms error of 2 mRy which is inside the noise of their calculation (as can be seen by comparing their results for the equivalent BZ points K and U).

The FS showed a very clear separation between the calculations with the f states included and those with the f states excluded. The two FS resulting from the calculations (c) and (d) with the f states included and with the configuration varied were close to identical. (This tends to give one confidence that these results will not differ greatly from a fully-self-consistent calculation.) The two FS for the f-states-removed calculations give some index of the small but observable sensitivity to exchange approximation of the underlying transition-element band structure. Thus the situation regarding the exchange appears to be a very fortunate one. In the transition metals, the plane wave bands are relatively insensitive to the exchange approximation whereas the d bands are more sensitive. Thus, the adjustment of the exchange parameter merely places the d bands properly relative to the plane-wave bands. In the case of thorium, the d bands are so broad as to exhibit little sensitivity to exchange. Thus, we are back to the same situation as in the transition metals except that here the exchange parameter adjusts positions of the f bands.

Comparing the results of the two calculations done with the f-states removed [(a) and (b)], we find that for the two hole surfaces (the superegg and the dumbbell), decreasing the exchange scale factor α has the effect of diminishing the size of the superegg and increasing that of the dumbbell. (Note that this is in the direction of improving agreement with the experimental data.) The electron surface—the lungs—is generally unchanged except for a slight increase in height which is compensated by an increased separation of the lobes resulting in decreased areas for the $\alpha = \frac{2}{3}$ calculation. These, however, are all very minor changes. This supports the earlier observation that the effect of changing α is to move the f states relative to the remaining bands. Thus the parameter α mainly affects these bands and their Fermi surface via the f states and their hybridization with these bands.

Having thus (briefly) described the effects of assumed configuration and exchange approximation, we examine the effect on the Fermi surface of including or omitting the f states. This effect is also found to be small but larger than that due to change of configuration or exchange. The effect on the hole surfaces is to move volume from the superegg to the dumbbell. The superegg shows somewhat more structure in addition to being smaller. The dumbbell is increased in size primarily on the ball portion—the rod section toward L remaining relatively unchanged. The electron surface (the lungs) is not centered on a high-symmetry point but on a line, and thus can change its position. The inclusion of the f states moves this surface slightly in the direction of Γ. The tube which connects the two lobes across the Σ line is reduced in size. The lobes themselves are taller and narrower. Qualitatively, these changes are all in the correct direction to improve the agreement between theory and experiment, as we shall see.

III. COMPARISON WITH EXPERIMENT

The first dHvA experiment[5] on Th metal was interpreted in terms of a Fermi-surface model consisting of a nearly spherical piece at the center of the BZ and a set of six closed segments located along [100] axes at the symmetry points X. More recently, highly resolved data[6] on a much higher-purity sample showed a low-frequency branch ≈ 2.5 MG in addition to the two relatively narrow bands at 9.5–14 and 19–25 MG found earlier.[5] As noted above, the Gupta and Loucks Fermi surface (cf. Fig. 1) based on the localized model is

in reasonable agreement with experiment. As such it served admirably as an aid in sorting out the experimental data.

For the two calculations with the f states retained [calculations (c) and (d) described above], a very careful calculation of the extremal orbit areas was made using orbit-tracing routines coupled with the RAPW method.[12] These areas are related to the de Haas–van Alphen frequencies F (in megagauss) by

$$F = 374.1A, \tag{1}$$

where A is in a. u.^{2}. This permits us to make detailed orbit-by-orbit comparisons of the theroetical predictions with the experimentally obtained dHvA frequencies. It was found that the d^2s^2 calculation (c) did not show an adequate degree of anisotropy for the Γ-centered hole cube although all areas were reasonably acceptable. The d^3s^1 calculation (d) gave more reasonable anisotropy for this surface and is thus presented as the calculted results.

Table II presents the comparison of the various calculated and observed extremal orbit cross-sectional areas on the lungs, dumbbell, and superegg "cube" surfaces following the notation of Boyle and Gold.[6] The agreement between the results of this calculation [calculation (d)] and all the experimentally observed areas is seen to be excellent provided that the experimental orbits labeled c and d on Fig. 1 of Boyle and Gold[6] are interchanged. The effect of including the f states is to reduce the largest discrepancies on the hole surfaces found in the f-states-excluded calculation from over 100% to less than 15%. As a more quantitative measure of the area differences between theory and experiment we have calculated a mean-square deviation,

$$\sigma \equiv \sigma_{\rm rms}/\bar{A}, \tag{2}$$

where

$$\bar{A} = N^{-1}\sum A_i^{\rm expt} \tag{3}$$

and

$$\sigma_{\rm rms}^2 = N^{-1}\sum (A_i^{\rm calc} - A_i^{\rm expt})^2 \tag{4}$$

for the different FS sections: for the lungs, $\sigma_L = 0.12$ for our calculation (vs 0.10 for the GL result); for the dumbbell, $\sigma_D = 0.067$ (vs 0.30 for GL); and for the superegg, $\sigma_E = 0.031$ (vs 0.67 for GL).

Table II also compares our calculated effective-mass values $m^*_{\rm calc}$ with the few experimental results available from the dHvA data. We find reasonable enhancement factors, $\lambda = 0.4$–0.7, due to electron-phonon dressing out of the "bare," or non-interacting electron values of m^*—again provided that the experimental[6] labeling of orbits c and d are interchanged.

In several of our area calculations, the Fermi energy was set at our earlier value of 0.5548 Ry rather than at the actual calculated Fermi energy of 0.5540 Ry. [On this energy scale, the bottom of the band appears at $E(\Gamma_6^+) = 0.1886$ Ry.] This small error revealed an interesting point about the electron lung surfaces in that the orbit L disappeared at the higher E_F value because the lungs from different directions touched. It is very well possible

TABLE II. Calculated and experimental values of the de Haas–van Alphen areas and masses in Th metal.

Orbit	Surface	Field direction	A (Calc.)	A (Expt.)	$\lvert m^*\rvert$ Expt.	m^* (Calc.)
A	Lung	[110]	0.0042	0.0067		0.20
B	Dumbell	[110]	0.0332	0.0361		−0.37
C	Lung	[110]	0.0364	0.0425		0.67
D	Lung	[110]	0.0222[a]	0.0257	0.58 ± 0.01	0.44
E	Dumbell	[110]	0.0499	0.0535		−0.41
F	Cube	[110]	0.0646	0.0670		−0.72
G	Lung	[111]	0.0809[a]			0.43
H	Dumbell	[111]	0.0256	0.0291		−0.27
I	Lung	[111]	0.0292[a]	0.0313		0.40
J	Dumbell	[111]	0.0584	0.0599		−0.48
K	Cube	[111]	0.0651	0.0672		−0.69
L	Lung	[100]	0.0265	0.0267	0.66 ± 0.03	0.55
M	Lung	[001]	0.0300	0.0315	0.58 ± 0.03	0.34
N	Cube	[001]	0.0577	0.0591	0.75 ± 0.03	−0.55
P	Lung	[001]	0.0584			0.71
Q	Dumbell	[001]	0.0584[a]			−0.81

[a]Estimated from a calculation for $E_F = 0.5548$ Ry instead of from the calculated $E_F = 0.5540$ Ry. [On the energy scale, the bottom of the band occurs at $E(\Gamma_6^+) = 0.1886$ Ry.]

that this would actually occur if Th were to be studied under pressure, a conclusion which follows from the following argument. The lungs themselves are almost independent of the presence of the f resonance, but the hole cube and dumbbell are quite sensitive to it. As one applies pressure (decreases the lattice constant) the f-state resonance will be broadened, and thus the f resonance will have an increased effect at the Fermi surface. From the discussion in Sec. II of the differences between the itinerant and localized models, one sees that the major effect will be for the hole cube to shrink and the dumbbells to grow. Furthermore, because of the lattice contraction, it is more likely that the dumbbells will grow more rapidly than the cube will shrink, thus causing an increase in the Fermi energy. In this argument, we have neglected the changes associated with the lungs directly due to the lattice contraction. This is done because the lungs arise from hybridized plane-wave and d states where the d states are so strongly overlapping that one might expect them to scale much like plane-wave states. Thus, one would expect the lungs to merely scale with the Brillouin-zone size.

The striking agreement seen in this work between theory and experiment is only obtained when the f states are treated as itinerant and are included in the band calculations even though these f bands lie well above the Fermi energy. Furthermore, it is seen that the underlying transition-metal band structure is quite insensitive to variations of configuration or exchange parameter α because the d states have become so extended as to no longer exhibit the sensitivity seen in the lighter transition metals. (This has motivated the use of a pseudopotential for Th with some success.[13]) Only the f orbitals exhibit any degree of sensitivity so that once the position (and thus width) of the f resonance is properly placed, one should have an accurate band structure. These results provide strong evidence for the view of the occupied $5f$ electron states in the light actinides are itinerant in character and are describable by the band model—in sharp contrast with the case of $4f$ electrons in metals.

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