Pressure dependence of the Fermi surface of Th†

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(Received 20 June 1977)

We report measurements of the pressure dependence of all three sheets of the Fermi surface of thorium. All of the cross-sectional areas investigated are found to *decrease* as the interatomic distance is diminished. This behavior is completely unprecedented for a cubic material and indicates that Th becomes less metallic with decreasing lattice spacing. We compare these results with calculations in which the unoccupied $5f$ electron bands are treated as itinerant and with a localized model ($5f$ states removed). While the itinerant model gives better normal-volume results as pointed out by Koelling and Freeman, the pressure results are only semiqualitatively reproduced by either model.

I. INTRODUCTION

The nature of the $5f$ electrons in the actinides has long been a topic of discussion and of a certain amount of controversy. Although it is tempting to look at the $5f$ series by analogy with the $4f$ rare-earth series, considerable experimental evidence points to itinerant nature for the $5f$ electrons in the early part (up to about Cm) of the series.[1,2] Detailed Fermi-surface data exist[3] only for the first member of the series, Th. Two Fermi-surface cross sections have been reported[4] for α-uranium. The Fermi surface of Th is relatively simple consisting of two hole sheets and a compensating electron sheet. The first hole sheet is centered at the point Γ of the fcc Brillouin zone and resembles a rounded cube (the "superegg"). The second hole surface is a distorted "dumbbell" centered at L and oriented along the [111] direction. The electron sheets, called the "lungs," are located within the Brillouin zone along the Σ axis. Gupta and Loucks[5] performed a relativistic augmented-plane-wave (RAPW) calculation with full Slater exchange in which they artificially removed the $5f$ bands. This "localized $5f$" model gave a reasonable qualitative picture for the observed Fermi surface but failed quantitatively to give the correct dimensions for the cross sections, particularly of the hole sheets.

Koelling and Freeman showed[6] that treatment of the $5f$ electrons as itinerant made very substantial improvement in the fidelity of the band-structure description to experiment. They made several predictions as to the effect that pressure would have on the Fermi surface. In particular they predicted that the superegg would decrease and the dumbbells would grow with increasing pressure. These effects are related to the expected broadening of the f resonance as the lattice contracts. The electron lungs were relatively unaffected by the f resonance so were predicted to increase in size in step with the Brillouin zone as the lattice contracts.

These predictions of Koelling and Freeman, coupled with the availability of much superior single-crystal Th than heretofore available, prompted us to initiate measurements of the pressure dependence of the Fermi surface of Th. We anticipated that the pressure dependence of the Fermi surface might be sensitive to whether a localized or itinerant $5f$ model were used. This possibility added to our interest in the pressure dependence of the electronic structure of Th.

In Sec. II we describe our experimental procedure. Section III describes the calculational approaches employed and Sec. IV discusses our results and conclusions.

II. EXPERIMENTAL

Samples were ~1-mm-diam by 2-mm-long cylinders cut by spark erosion from a thorium rod that had been electrotransport purified during a developmental program sponsored by the National Aeronautic and Space Administration.[7] The rod was heated for 144 h under a pressure of 4×10^{-12} Torr and large single crystals were prepared by a temperature cycling technique described by Peterson and Schmidt.[8] The residual-resistance ratio (resistance at 300 K to resistance at 4 K) of this rod was ~2000.

Fermi-surface cross sections were determined from measurements of de Haas–van Alphen (dHvA)

frequencies using field-modulation techniques[9] in a 55-kOe solenoid near 1.2 K. Pressure derivatives were determined using one or more of three techniques as appropriate: (i) direct measurements of the frequency made as a function of hydrostatic pressure to ~4 kbar generated[10] by isobaric freezing of He, (ii) measurement of the shift in position of a single dHvA oscillation in fluid He (fluid helium phase shift),[11] and (iii) measurement of the shift in dHvA phase in solid He (solid He phase shift technique).[12] In the latter two techniques advantage is taken of the high ratios of the dHvA frequency F to field B so that the pressure derivative of F, $d\ln F/dP$, is given by $d\ln F/dP = B^{-1}\Delta H/\Delta P$. Here ΔH is the shift in field position of an individual oscillation with a pressure increment ΔP.

The experimental results are summarized in Table I for cross sections with fields along the principal field directions. We employ the orbit designations used by Boyle and Gold[3] as well as the sheet nomenclature of "superegg" for the Γ-centered hole sheet, "dumbbell" for the L-centered hole sheet and "lung" for the electron sheet on the Σ axis. Th is a face-centered-cubic valence four metal so the volumes of the hole sheets are equal to the volume of the electron sheets, i.e., it is compensated. The most striking feature of the data in Table I is that all the pressure derivatives are negative. In a cubic material, as the volume decreases, the Brillouin zone increases and the same fraction of the zone must remain filled unless carriers are being created or destroyed. Therefore, the expected result and that observed in many materials is that the Fermi surface scales at a rate given by $\frac{2}{3}K_T$ where K_T is the volume compressibility. The surprising result that all the cross sections decrease is unprecedented for a cubic material and indicates that the material is becoming less metallic with increasing pressure. It must be pointed out that this is not yet demonstrated unequivocally since it is possible that the largest cross sections of the dumbbell and the lung might be increasing with pressure. The frequencies corresponding to these cross sections have never been reported.

III. BAND STRUCTURE CONSIDERATIONS

Gupta and Loucks[5] achieved a qualitative fit to the original dHvA data of Boyle and Gold[3] by considering the $5f$ band to be highly localized above the Fermi energy so that they could ignore it completely in their calculation. Koelling and Freeman[6] subsequently showed that the qualitative agreement found by Gupta and Loucks (GL) could be substantially improved by treating the $5f$ electrons as itinerant. Koelling and Freeman (KF) compared the agreements of the two models with experiment by calculation of a mean square deviation between calculated and observed values for the various Fermi surface sections. For the lungs they found 0.12 vs 0.10 for GL; for the dumbbell, 0.067 vs 0.30 for GL; and for the superegg, 0.031 vs 0.67 for GL.

In conjunction with their comparison of the agreement of the two models for the $5f$ electrons with Fermi surface data, KF made qualitative predictions for the behavior of their band structure as the volume is decreased. These predictions were

TABLE I. Pressure dependence of Fermi-surface cross sections of Th.

Cross section	Orientation	Frequency (10^6 G)	$d\ln F/dP$ (10^{-4} kbar^{-1})
Hole superegg (N)	[100]	22.1	−38 (±4) [a] −40 (±1.0) [b]
Electron lung (L)	[100]	10	−4.4 (±0.4) [c]
Hole superegg (F)	[110]	24.7	−38 (±4) [a]
Electron lung (C)	[110]	9.6	−3.4 (±0.3) [c]
Electron lung (A)	[110]	2.014	−50 (±10) [a] −60 (±10) [b]
Hole dumbbell (E)	[110]	19.8	−12 (±7) [a] −11 (±2) [c] −13 (±5) [b]
Hole dumbbell (H)	[111]	10.9×10^6	−39 (±5) [a]
Electron lung (I)	[111]	11.6×10^6	−14 (±6) [a]

[a] Fluid He phase shift.
[b] Direct frequency measurement in solid He.
[c] Solid He phase shift.

based on the importance of the presence of the f resonances. The lungs were expected to be unaffected while the hole sheets were quite sensitive to the presence of the f resonance. Qualitatively, KF predicted a decrease in the size of the superegg, compensated by an increase in the dumbbell, while the lungs were expected to more or less scale with the Brillouin zone.

Inspection of the pressure derivatives given in Table I shows that these qualitative predictions are only partially fulfilled. We have therefore done a complete band structure and determination of the Fermi surface at a reduced lattice constant corresponding to 9.2 kbar. This change in lattice constant is enough to effect changes of sufficient magnitude to be well outside the calculational uncertainty but still small enough (~0.5%) so that the overlapping charge density (OCD) model might still be used.

Two additional potentials were created in addition to the one originally used by Koelling and Freeman (which we will identify as KF). These two potentials were constructed for the reduced lattice constant ($a = 9.56$ a.u. versus the normal volume value of $a = 9.6085$ a.u.) utilizing the OCD model for the atomic configurations Th: $f^0d^3s^1$ ($R1$) and Th: $f^{0.2}d^{2.8}s^1$ ($R2$). The latter was included to simulate the effect of increased f-orbital occupancy. The Kohn-Sham-Gaspar exchange approximation was used throughout. The warped-muffin-tin shape approximation was applied: the potential was spherically averaged within the muffin-tin spheres but the full model potential was used within the interstitial region. For each potential the bands, the density of states, and thus the Fermi energy were recalculated utilizing a variant of the relativistic augmented plane wave (RAPW) method,[13] Fourier series fitting of the bands, and a tetrahedron-based density-of-states code. Once the Fermi energy was found for the potential, orbits were traced using a direct RAPW orbit tracer in the same way as in KF. That is, at any point near the Fermi surface, the RAPW code calculated the eigenvalue and its gradient. These were then used to find the point on the Fermi surface and then to calculate the additional area and mass increment for the orbit. The quantity dA/dk_H was also calculated and it was insured that one actually had calculated for an extremal orbit. This was quite time consuming for Th as many of the orbits are not pinned by symmetry requirements. Thus it was necessary to locate the extremal orbit *for each potential*. The results of these calculations are tabulated in Table II where they are compared with the experimentally observed frequencies. Note that most of the orbits change in the observed manner with a decrease in lattice constant *without* increasing the assumed f character ($R1$). This situation can be improved by also increasing the f character ($R2$)—especially orbit E on the dumbbell but at the expense of worsening the agreement for the electron lung surface. From the observations that $R1$ produced the most of the observed trends, it was suspected that the dominant effect of pressure had little to do with the presence of the f resonance. Thus we performed calculations with all three potentials (for the superegg and dumbbell only) with the f resonance removed or shifted up 0.3 Ry. The general trend remained. This is very good evidence that what is being observed is a change in the s-d hybridization affecting the overlap of the bands reminiscent of the situation in fcc Yb where a gap is opened up by

TABLE II. Comparison of observed and calculated Fermi-surface areas for Th in units of 10^6 G. Experimental values were obtained from lower pressures by linear extrapolation.

			Experiment		Calculated		
Surface	Orbit	Direction	(Normal volume)	(~ 9 kbar)	(Normal volume)	($R1$) (~ 9 kbar)	($R2$) (~ 9 kbar)
Superegg	N	[100]	22.1	20.3	21.1	20.3	20.0
	F	[110]	24.7	23.8	23.5	22.6	22.3
	K	[111]	25.2	•••	23.7	22.9	22.5
Dumbbell	B	[110]	13.5	•••	12.0	11.8	10.9
	E	[110]	19.8	19.6	18.3	18.6	17.6
	H	[111]	10.9	10.5	9.3	9.2	8.5
	J	[111]	22.4	•••	21.4	21.9	20.7
	Q	[211]	•••	•••	49.3	44.3	42.7
Lung	A	[110]	2.014	1.91	1.74	1.43	1.8
	C	[110]	9.6	9.57	8.7	8.9	9.6
	D	[110]	15.9	•••	14.3	13.8	a
	L	[100]	10	9.96	10.2	11.2	11.2

[a] This orbit bridges across in this potential and does not exist.

pressure.[14]

To see whether the idea that the f-resonance broadening increased the occupied f-orbital character, we tabulated in Table III the occupied l character. By comparing $R1$ with KF, we see that there is an overall increase in charge within the sphere due to the decrease in size of the unit cell. By just considering a volume scaling, one sees that there is still a modest increase in the d and f character. By comparing $R1$ and $R2$, we see that the s and d characters are fairly stable while the p and f characters are modified by the configuration change (i.e., self consistency).

We believe this is the limit of the information one can obtain from the OCD model. Further analysis will have to await self-consistent calculations.

TABLE III. Occupied l character (from a sum of $j = l \pm \frac{1}{2}$ components) within the spheres of radius R = 3.275 a.u.

	s	p	d	f
KF	0.40	0.19	1.73	0.33
$R1$	0.41	0.21	1.78	0.37
$R2$	0.40	0.25	1.77	0.33

IV. DISCUSSION

The experimental and calculational results indicate that both the calculation with itinerant f bands and the "f bands removed" or localized f-states calculation give qualitative agreement with experiment. Both models tend to reproduce the unexpected experimental finding of a general decrease in the size of the cross sections of both hole and electron sheets with pressure and imply that the dominant effect of pressure is to modify the s-d hybridization. The work of Koelling and Freeman showed that the itinerant f-band model gave a better fit to the normal-volume Fermi-surface data but there is really little to choose between the models as far as the pressure dependence of the cross sections is concerned—both give semi-qualitative agreement with our observations.

It would appear that a more sophisticated treatment of the band structure will be required to give a quantitative picture of the Fermi surface as a function of interatomic spacing. Very recent work[15] on Gd gives indications that self-consistent treatments may be necessary for the $4f$ series as the d orbitals are more extended than the atomic orbitals because one is at the bottom of the band. This may well prove to be the case for actinides as one is at the bottom of the f bands. This would enhance the utility of the band picture in the light actinides by increasing bandwidths and lowering intra-atomic Coulomb interactions.

ACKNOWLEDGMENTS

We are indebted to R. L. White for technical assistance, to Professor A. J. Freeman for suggesting the problem and to Dr. A. C. Switendick for helpful comments.

†Work supported by the U.S. ERDA under Contract No. AT(29-1)-789.

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