Fermi surface of α-uranium

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(Received 24 September 1979)

Pressures above 8 kbar have been shown to quench the low-temperature phase changes in U permitting retention of the α-U phase to liquid-He temperatures. Field-modulation de Haas–van Alphen measurements are then possible at pressures >8 kbar for fields in the 50–100-kOe range. The angular variations of four frequencies in the range of $(1–2)\times 10^7$ G have been determined in the three inequivalent principal planes. All frequencies appear to arise from open sheets of the Fermi surface. Effective masses were measured for the minimum-area directions. These results are compared with a recent band-structure calculation of Freeman, Koelling, and Watson-Yang.

I. INTRODUCTION

In spite of the large amount of interest in, and the technological significance of, uranium, very little has been definitively established as to the detailed electronic structure of α-U. Direct experimental determinations of the Fermi surface and other single-crystal-related properties have been thwarted by several low-temperature phase transitions[1] that occur on cooling α-U below 43 K. Furthermore, the low symmetry of the α-U structure and the importance of relativistic effects when coupled with the paucity of direct experimental data had effectively discouraged any realistic band calculations in the proper structure until the present study was made known.[2] This is unfortunate in that ongoing concern and controversy on the degree of localization of the $5f$ electrons in the early actinides can probably best be resolved by a combination of band calculational modeling with complementary optical and Fermi-surface data. In this study we present the first detailed determination of the Fermi surface of an elemental actinide with a partially filled $5f$ shell by means of de Haas–van Alphen (dHvA) techniques.

The quality of crystals available at present and the pressures necessary to elude the phase transitions require that most of the measurements be made at fields in excess of 80 kG at 1 K and at pressures >8 kbar. This coupled with the low symmetry of the α-U lattice so that at least three symmetry planes must be scanned to adequately cover the Brillouin zone makes the experimental determination of the Fermi surface both difficult and tedious. We have obtained what appears to be an adequate data set[3] to make a quantitative comparison with band calculations and present these data and a preliminary comparison with a very recent RAPW band calculation of Freeman, Koelling, and Watson-Yang[4] in Sec. III. In Sec. II we present the experimental details.

II. EXPERIMENTAL

The samples were cut from the same material used in our original investigation[2] which were grown by recrystallization within the α phase. Here, however, the dimensions were much smaller, ~0.5-mm diameter by 2-mm-long cylinders cut by spark erosion along the three principal orientations of the orthorhombic lattice. These samples fit within a 3200 turn counter-wound pickup coil which in turn fits into the $\frac{1}{8}$-in. bore of the pressure vessel. The coil axis is orthogonal to the bore of this pressure vessel. The coils were free-standing 0.0005-in. diameter Cu wire impregnated with epoxy, balanced to within one turn. The sample was oriented by back reflection Laue techniques so the rotation plane of the 100-kOe split superconducting magnet would be in a principal plane of the crystal. Because of the orthorhombic symmetry and the geometry employed, six rotations were required to completely cover the three orthogonal symmetry planes.

Pressures to ~9.5 kbar were generated by very careful isobaric freezing of He around the coil-sample assembly.[5] The sample was glued to one end of the coil with GE 7031 varnish. With sufficient care at least 10 pressure cycles were possible with this arrangement before the coils were damaged.

This geometry was found to be necessary because of the combination of (i) the high effective masses of the frequencies involved, (ii) the poor filling factor of the Helmholz geometry required if the usual exterior-to-pressure-vessel arrangement were used, and (iii) the modest quality of the crystal which must be recrystallized from the

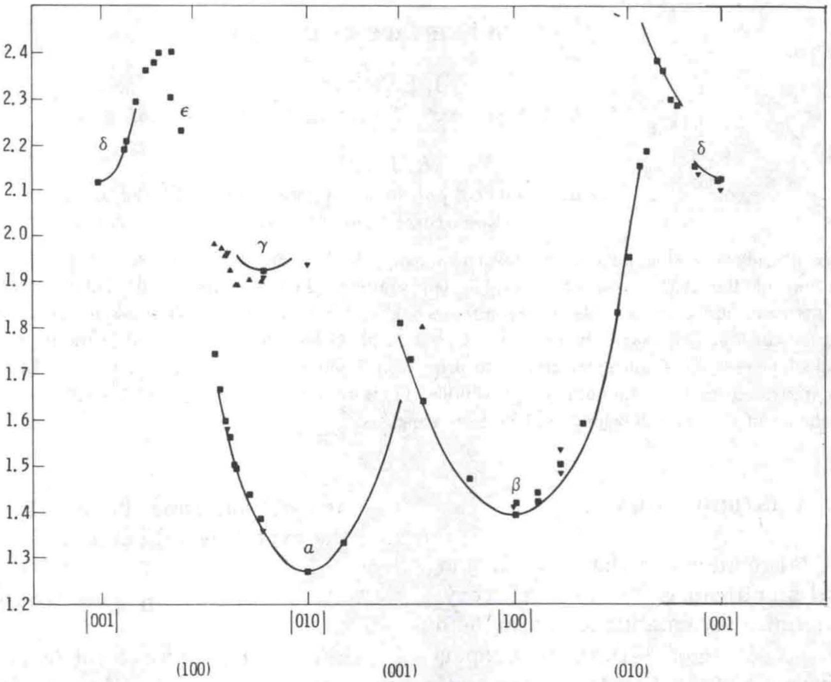

FIG. 1. dHvA spectrum for α-U in the three principal planes. Complementary methods of frequency F, determination denoted by symbols as indicated: ——, rotation pattern; ■, direct frequency; ▲, beat pattern; ▼, Fourier. The square brackets $[h,k,l]$ refer to direction; the parentheses, to planes.

high-temperature bcc phase.

De Haas–van Alphen (dHvA) frequencies were obtained using the field-modulation technique[6] with modulation amplitudes to ~600-G generated exterior to the pressure vessel. Frequencies were obtained by direct period measurement, from rotational sweeps in the principal crystallographic planes at constant field and from Fourier analyses

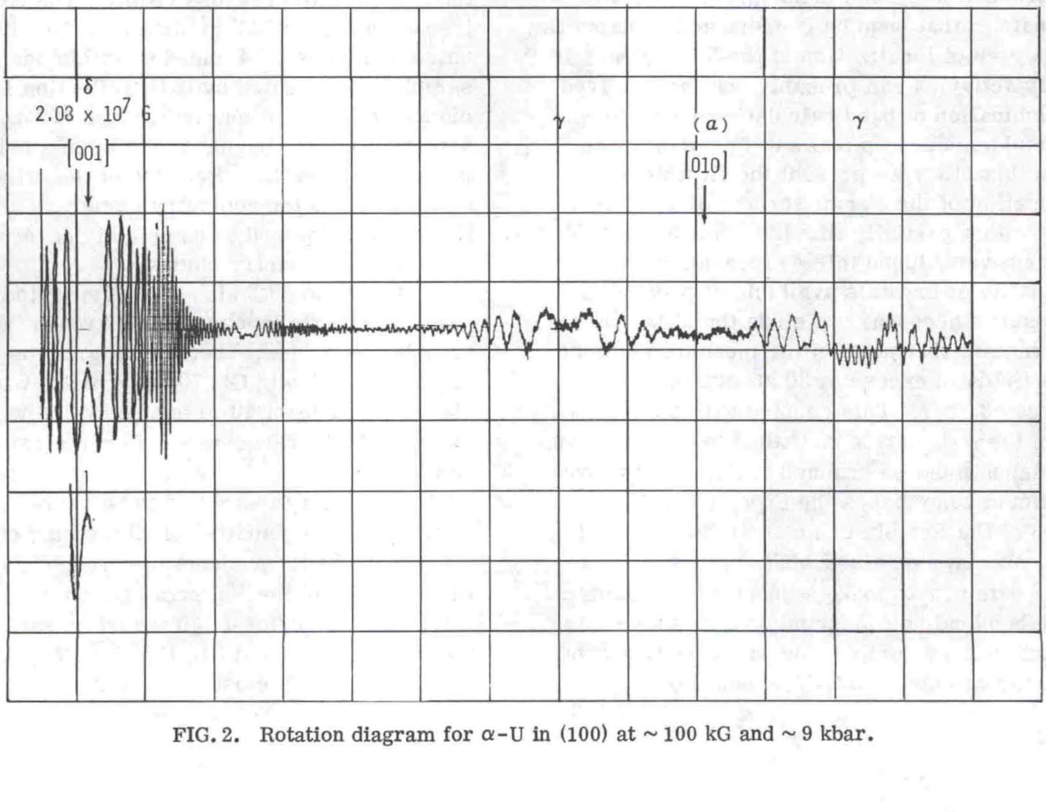

FIG. 2. Rotation diagram for α-U in (100) at ~ 100 kG and ~ 9 kbar.

TABLE I. Effective-mass ratios of various sheets of the Fermi surface of U for minimum-area field directions. Data were taken near 9.0 kbar. The numbers shown in parentheses are conservative estimates of the uncertainties in the last place shown of the values quoted for the frequencies and masses.

Fermi-surface sheet	Field direction	Frequency (10^6G)	Effective-mass ratio
α	[010]	1.269 (5)	0.91 (5)
β	[100]	1.39 (1)	0.90 (7)
γ	70° from [001] in (100)	1.90 (2)	1.8 (1)
δ	[001]	2.08 (2)	1.8 (1)

of digitized field sweeps at constant angle. Effective masses were obtained from the amplitude of the dHvA oscillations between 1 and 2 K.

III. RESULTS AND DISCUSSION

Our cross-sectional area data are given in Fig. 1 in terms of the dHvA frequencies as a function of magnetic field direction in each of the three principal crystallographic planes. An example of a rotation is shown in Fig. 2. These data are for H in the (100) plane at ~9 kbar and ~100 kG. In all, at least five separate frequencies could be separated and are denoted in order of increasing magnitude by α, β, etc. These frequencies were determined by direct period measurement, from beat pattern analyses, from Fourier analyses, and from angular rotations at constant field. The agreement in the various determinations is well within the attendant uncertainties involved. The effective mass ratios of several of the sheets for their minimum observed area directions are given in Table I.

None of the frequencies observed correspond to closed sheets of the Fermi surface. The α frequency varies with angle essentially as a cylinder (i.e., $f=f_0/\cos\theta$, where f_0 is the value at the minimum, and θ is the angle between H and the minimum direction) while the β frequency varies considerably slower than this rate and the δ frequency much faster. The γ and ϵ frequencies are weak and can be followed for only a short angular distance. The ϵ frequency may in fact be an extension of either the γ or α branches.

Freeman, Koelling, and Watson-Yang[4] have performed a band-structure calculation of α-U using the relativistic linear augmented plane wave method assuming an $f^3d^2s^1$ configuration. This calculation gives two bands crossing the Fermi level. The 6th-band hole surface, shown in Fig. 3, is open in the [001] direction. This surface resembles an undulating tube with a waist at the top of the zone (symmetry point T in the Brillouin zone) and gives rise to two extremal closed electron trajectories for $\vec{H}\|[001]$ centered at the points T and Y. The 7th band gives rise to a complicated electron sheet which is also open in the [001] direction (see Fig. 4). This complex sheet allows closed electron trajectories for fields along all of the principal axes.

We can find fairly reasonable semiquantitative correspondence of the observed frequencies with this calculated Fermi surface. There are no predicted closed sheets, as observed. The approximate sizes of the frequencies (near 2×10^7 G) observed are in good general agreement with those predicted by the calculation as shown graphically in Fig. 4(d), and the general topology seems to be consistent. Detailed comparison awaits the completion of the calculation of the extremal orbits supported by these sheets in the various crystallographic directions. However, we can already make some semiquantitative comparisons with the information given in Figs. 3 and 4 realizing that additional experimental information may result in changes in the present identifications.

Consider first the case for $\vec{H}\|[001]$. The model

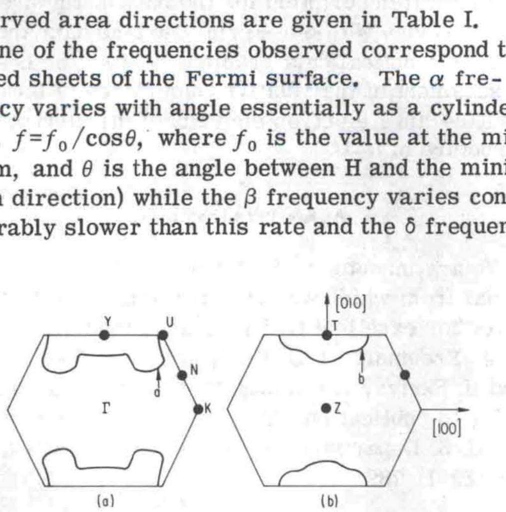

FIG. 3. α-U band 6-hole surface and Brillouin-zone cross section in the (001) plane (after Freemen *et al.*): (a) at $z=0.0\pi/c$ and (b) at $x=1.0\pi/c$.

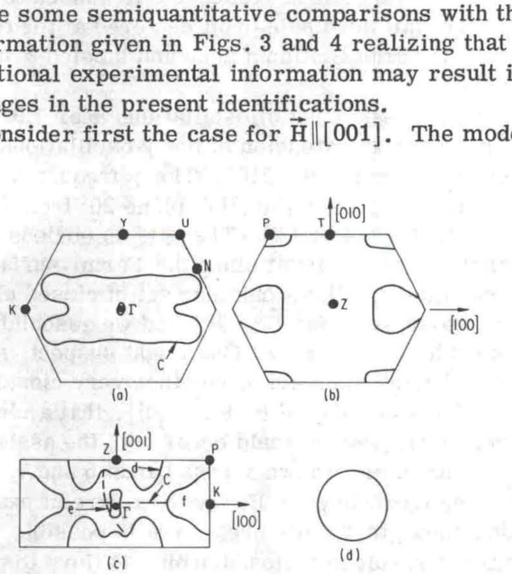

FIG. 4. α-U band 7-electron surface and Brillouin-zone cross sections (after Freeman *et al.*): (a) (001) plane at $z=0.0\pi/c$, (b) (001) plane at $z=1.0\pi/c$, (c) (010) plane at $y=0.0\pi/b$, and (d) cross-sectional area corresponding to a frequency of 2.1×10^7 G, using same scale as (a), (b), and (c).

of Freeman *et al.* indicates three possible extremal cross-sectional areas; two on band 6 labeled a and b in Fig. 3, and one on band 7 labeled c in Fig. 4. Orbits b and c are waist orbits whose frequencies would increase faster with angle than $(\cos\theta)^{-1}$. The opposite is true for orbit a. Since frequency δ observed at [001] increases faster than $(\cos\theta)^{-1}$, we can tentatively associate it with orbits b or c. Figure 4(d) shows a cross-sectional area corresponding to a frequency of 2.1×10^7 G. It very closely corresponds to the area of the orbit labeled b on band 6 and thus we assume that frequency δ can be associated with the waist orbit on the band 6 hole surface centered at the point T in the Brillouin zone (symmetry labels are after Koster[7] and Jones[8]). Failure to observe orbits a or c is not considered a serious discrepancy since they would likely have an effective mass larger than frequency δ, and thus be unobservable under existing conditions.

For $\vec{H}\parallel[100]$ we observe a single frequency β, which increases with angle at a rate slower than for a cylinder. We assign this frequency to the orbit labeled e in Fig. 4(c) on the band 7 electron sheet centered at Γ which is expected to increase slower than $(\cos\theta)^{-1}$. This assignment requires a small adjustment to eliminate the small pocket at the center of the zone but this is probably well within the calculational uncertainty.

The strongest frequency observed in α-U is frequency α which has a minimum value at $\vec{H}\parallel[010]$. These α oscillations vary with angle nearly as a cylinder, and so it is reasonable to associate them with the flat sided hole orbit centered at the top (point Z) of the Brillouin zone and labeled d in Fig. 4(c).

A much weaker set of oscillations near 1.9×10^7 G, probably an extension of the γ oscillations, is also observed for $\vec{H}\parallel[010]$. The γ frequency has a minimum value in the (100) plane 20° from [010] (refer to Figs. 1 and 2). There is no obvious assignment for this orbit since the Fermi-surface, as calculated, allows only one set of closed electron trajectories for $\vec{H}\parallel[010]$ and we associate these with frequency α. One might suspect, since bands 6 and 7 approach each other very closely near the point labeled P [Fig. 4(b)], that a closed electron trajectory would occur with the assistance of magnetic breakdown across bands 6 and 7, yielding frequency γ. However, a careful examination shows that while breakdown is possible, it does not result in a closed orbit. Failure to predict the γ frequency is a serious failure of the model of Freeman *et al.* If it is not to be discarded (and we feel that there is sufficient qualitative agreement to deserve further consideration) then the bands must be modified enough so that the band 7 Fermi-surface touches the zone face near the N point in the zone. With sufficient juggling this would result in an additional hole orbit for $\vec{H}\parallel[010]$ which may in fact have a minimum frequency away from the [010] direction. This orbit should, however, be observed in the (001) plane as well. Such modification also creates an additional hole orbit centered at Y for $\vec{H}\parallel[001]$ which has not been observed but which would be expected to have a large m^*. On the other hand, it eliminates the currently predicted orbit c. This is the weakest part of the model of Freeman *et al.* It is hoped that it can be corrected with the above modification.

Another slightly disturbing feature of this model is our failure to find oscillations corresponding to the approximately [101] oriented arms shown in Fig. 4(c). It is likely that they also are of very large mass, but a detailed calculation bearing this out is necessary to make this argument really appealing. Also, if contact is indeed made with the zone boundary, this orbit may or may not exist.

We see that a reasonable semiquantitative picture for the Fermi surface of α-U seems to be emerging. Further refinement of the calculations will be required to assess additional agreement of this band calculation with our results.

Skriver has begun self-consistent band calculations on α-U which show some differences from those of Freeman, Koelling, and Watson-Yang. The data we have presented will be valuable in assessing the importance of self-consistency in this system and in choosing between the various band descriptions. The determination of the best theoretical description for the band-structure from comparisons with our Fermi-surface data and available optical data promise to offer the best assessment of the relative importance of localized vs itinerant f electron pictures of the electronic structure of α-U.

ACKNOWLEDGMENTS

We are indebted to E. Fisher for the α-U material from which we cut our crystals, to D. Overmyer for excellent technical assistance, and to A. J. Freeman, D. D. Koelling, T. J. Watson-Yang, and H. Skriver for discussions of their calculations prior to publication. This work was supported by the U. S. Department of Energy under Contract No. AT (29-1)-789.

*A U.S. Department of Energy facility.

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