ELECTRONIC STRUCTURE OF THORIUM METAL. I. RELATIVISTIC AUGMENTED-PLANE-WAVE CALCULATION*

R. P. Gupta
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010

and

T. L. Loucks†
Science Center, North American Rockwell Corporation, Thousand Oaks, California 91360
(Received 9 January 1969)

A theoretical Fermi-surface model is presented for Th. It is in qualitative agreement with the earlier experimental results of Thorsen et al., and with the more recent results of Boyle and Gold as presented in the following Letter. We conclude that Th is very similar to the fcc transition metals.

During the last few years there has been considerable effort devoted to understanding the electronic structure of the transition metals, and from ab initio energy-band calculations, experimental measurements, and, more recently, parametrized models has emerged a unified picture for these metals. In general one can think of a free-electron energy band combined with a more localized d band, and a certain amount of hybridization between the two. The width of the d band and its position relative to the free-electron band depend on the crystal structure and the position of the element in the periodic table, but broadly speaking all the transition metals of the same crystal structure have very similar energy bands (ignoring magnetic effects), the primary difference being in the location of the Fermi energy.

This is even true of the $4f$ rare-earth metals, with some understandable exceptions. For instance, all the heavy rare earths with hcp crystal structure have essentially the same energy bands and Fermi surfaces as their trivalent cousins the transition metals Sc and Y. The $4f$ levels in these rare earths are very narrow (the electrons are highly localized) and have energies well below the conduction band, and the outer electrons are hybridized s-d bands just as in the transition metals. Similar comparisons can be made between Yb and the "transition" metals Ca and Sr (divalent fcc), between Eu and Ba (divalent bcc), and between Pr, Nd, and La (trivalent dhcp). In La, the $4f$ band lies above the Fermi energy and consequently does not appreciably affect the s-d energy-band picture for the occupied states. An exception to these comparisons between rare-earth and transition metals is Ce; in this metal the $4f$ level is near the Fermi energy and this drastically alters its Fermi surface.

The purpose of this Letter is to point out that the lighter actinides fit into this same general picture. By analogy with the lanthanides we expect that the $5f$ level for the first few actinides will be above the Fermi energy. For the heavier ones with partially filled $5f$ shells this level should be below the conduction band. In both of these cases the electronic structure (especially the Fermi surface) should be very similar to isoelectronic transition metals having the same crystal structure. Presumably, as is the case with Ce, there will be at least one of the actinides in which the $5f$ level is near the Fermi energy and a comparison with the transition metals would not be meaningful.

In turning to the literature for possible confirmation of this view one is disappointed by two facts: Firstly, conventional Fermi-surface data are only available for one actinide, Th, and, secondly, none of the existing energy-band calculations (including an effort by one of the present authors) are in agreement with these data.

In this Letter we explain the origin of this disagreement and present new ab initio calculations for Th which are compatible with accepted results for fcc transition metals and which appear to be in qualitative agreement with the recent de Haas–van Alphen measurements reported by Boyle and Gold in the following Letter.[1]

The first energy-band calculation for Th of which we are aware was performed by Lehman.[2] This was a very early investigation (1959) and not really directed toward Fermi-surface information; the primary interest was in the effect of spin-orbit splitting on the d bands. More recently Keeton and Loucks[3] performed relativistic augmented-plane-wave (RAPW) calculations and found what they believed to be the s-d bands for Th.

The first experimental information on the Fermi surface became available in 1967 when Thorsen, Joseph, and Valby[4] observed the de Haas–van Alphen effect. Their results indicated a nearly spherical piece of Fermi surface at the center of the Brillouin zone and a set of six closed sigments located along the ⟨100⟩ axes at the symmetry points X. These results could not be explained on the basis of the free-electron model (a not very surprising fact). They were also not in accord with the two energy-band calculations cited above.[2,3]

As mentioned, Lehman's[2] calculation was for the d bands only, and for this reason one would not expect the Fermi surface information to be complete. On the other hand, the RAPW method has given reasonably accurate results in several previous applications.[5] The reason the results of Keeton and Loucks[3] were incorrect, however, was pointed out by Waber[6]; the $5f$ levels turned out to be in the middle of their d bands.

This points out a problem with energy-band calculations for $4f$ and $5f$ metals. It is well known that the s-d separation is sensitive to changes in potential, but fortunately the sensitivity is not too great. This is witnessed by the fact that in spite of the crude schemes frequently used for constructing potentials, energy-band calculations have nevertheless yielded accurate information in many instances. We are not so fortunate with the f levels. In calculations for Th[2] and the rare earths,[7] it has been found that the "position" of the f levels[8] is extremely sensitive to small potential changes. To eliminate this inconvenience we have decided to remove the f levels entirely by modifying the $l=3$ logarithmic derivative[5] so that no singularity exists. Experience has shown that this does not modify the actual s-d bands; it only moves the f levels out of the energy range of the conduction electrons. Our justification for doing this is simply that we are primarily interested in the Fermi surface, and since experimental evidence indicates that the f levels are well above (or below) the Fermi energy we force them out of the picture rather than attempting to adjust the potential with the same motivation.

Our results for Th are shown in Fig. 1. We used the RAPW method with the f levels removed as mentioned above. The results are entirely different from the earlier calculations[3] although one can see the effects of hybridization with the s band by comparing our results with the d bands of Lehman.[2] It is gratifying that our results are

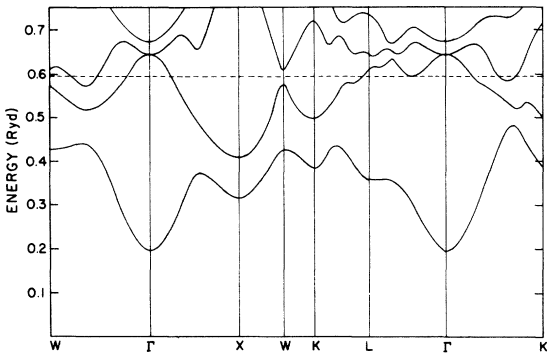

FIG. 1. Energy bands of thorium.

similar to several other existing calculations for fcc transition metals. One can compare, for instance, with the results for paramagnetic Fe[9] and Ni.[10] The primary differences are due to the increased importance of relativistic effects for the heavier metal ($Z=90$).

Our Fermi surface is shown in Fig. 2. There are three distinct segments: (1) a hole surface at the center of the Brillouin zone shaped like a rounded cube; (2) electron surfaces on the symmetry lines $\Gamma K\langle 110\rangle$ shaped like pairs of lungs; and (3) hole surfaces on the symmetry lines $\Gamma L\langle 111\rangle$, centered at L, shaped like dumbbells with triangular ends.

The rounded cube has been observed previously by Thorsen, Joseph, and Valby.[4] They presented de Haas–van Alphen periods which were associated with a nearly spherical Fermi surface segment located at the symmetry point Γ. We choose to call this a rounded cube rather than a nearly spherical surface in order to draw attention to its more cubical shape. Cubical Fermi surfaces are currently of great interest because opposite faces of these figures can "nest"[11] into one another. This can show up as Kohn-type anomalies in phonon and magnon spectra and can also influence the arrangement of any magnetic moments which might be present. For instance, if Th were doped with magnetic impurities of the same valency, it can be predicted that through indirect exchange coupling they would order in some periodic moment arrangement with the axis in the ⟨100⟩ directions and with a period fixed by the separation between the faces of the rounded cube. From Fig. 3 we see that this separation is about 3.8 (in units of $\pi/4a$), which yields an interlayer turn angle of approximately 86°.[12] If the magnetic impurities have a higher valency that Th, then the Fermi energy will be raised and the rounded-cube dimensions will increase, thus increasing

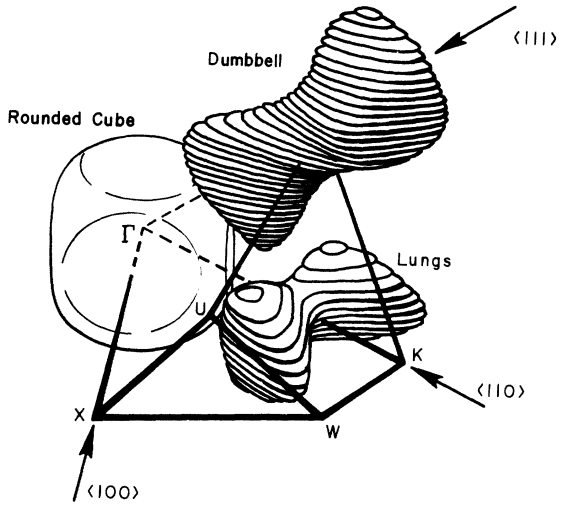

FIG. 2. Fermi surface of thorium.

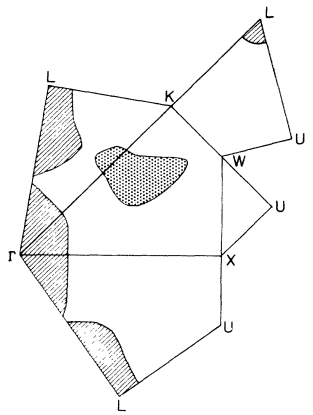

FIG. 3. Intersections of the Fermi surface with the faces of the Brillouin zone, with the holes lined and the electrons dotted.

the interlayer turn angle. Another possible manifestation of the rounded cube would be the presence of a Kohn-type anomaly in the phonon spectra approximately halfway to the zone edge in the ⟨100⟩ direction.

The other pieces of Fermi surface, the lungs and the dumbbells, yield a multitude of de Haas–van Alphen frequencies primarily in the range 5-25 MG. Thorsen, Joseph, and Valby[4] observed several signals of approximately this magnitude and tentatively identified them with a set of six ellipsoids located at the symmetry points X. We observe in the energy bands (Fig. 1) that this interpretation is unlikely since there are no levels near the Fermi energy at these symmetry points. On the other hand, the more recent data of Boyle and Gold indicate that the relevant sheets of the Fermi surface have a symmetry corresponding to that of the proposed lungs, i.e., surfaces along ΓK rather than along ΓX (see their paper for identification of orbits).

The agreement, even though qualitative, between our results and those of Boyle and Gold is very important, since it represents a definite step toward an understanding of the electronic structure of the actinides. Now we can definitely assert that the lighter actinides which do not have $5f$ bands near the Fermi energy are similar to the transition metals and can be described by the same hybridized s-d energy-band model. This understanding gives us a very strong vantage point for further study of the actinides. By comparison, the situation in the lanthanides has not been nearly as good. For these metals most of the information relating to the Fermi surface has been quite indirect[7] and the lack of experimental Fermi-surface data has made progress very tedious. However, the success we have found for thorium not only opens the way for further understanding of the actinides but also provides further confidence in the theoretical results for the lanthanides since the same techniques have been applied.

---

*Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

†Alfred P. Sloan Research Fellow.

[1]D. Boyle and A. V. Gold, following Letter [Phys. Rev. Letters 22, 461 (1969)].

[2]Guy W. Lehman, Phys. Rev. 116, 846 (1959).

[3]S. C. Keeton and T. L. Loucks, Phys. Rev. 146, 429 (1966).

[4]A. C. Thorsen, A. S. Joseph, and L. E. Valby, Phys. Rev. 162, 574 (1967).

[5]T. L. Loucks, Augmented Plane Wave Method (W. A. Benjamin, Inc., New York, 1967).

[6]J. Waber, private communication.

[7]S. C. Keeton and T. L. Loucks, Phys. Rev. 168, 672 (1968); O. Krøgh Andersen and T. L. Loucks, Phys. Rev. 167, 551 (1968); G. S. Fleming, S. H. Liu, and T. L. Loucks, Phys. Rev. Letters 21, 1524 (1968).

[8]The actual position of the $4f$'s does not depend on the potential for the conduction electrons but rather on terms not usually present in the energy-band Hamiltonian.

[9]J. H. Wood, Phys. Rev. 126, 519 (1962).

[10]L. F. Mattheiss, Phys. Rev. 134, A970 (1964); L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966); S. Wakoh and J. Yamashita, J. Phys. Soc. Japan 18, 999 (1963), and 19, 1342 (1964).

[11]In addition to Ref. 7, also see W. E. Evenson, G. S. Fleming, and S. H. Liu, Phys. Rev. (to be published); G. S. Fleming and T. L Loucks, Phys. Rev. 173, 685 (1968).

[12]H. R. Child, W. C. Koehler, and A. H. Millhouse, J. Appl. Phys. 39, 1329 (1968). These authors report neutron-diffraction results for rare-earth–thorium alloys which are interpreted in terms of short-range antiferromagnetic correlations. We are currently studying this more completely.

ELECTRONIC STRUCTURE OF THORIUM METAL. II. THE de HAAS–van ALPHEN EFFECT*

D. J. Boyle† and A. V. Gold‡
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010
(Received 9 January 1969)

High-resolution studies of the de Haas–van Alphen effect in thorium, although not yet complete, are found to provide strong support for the validity of a new model for the Fermi surface proposed by Gupta and Loucks in a companion paper.

Thorium is thus far the only metal in the actinide series for which experimental data exist relating to the details of the electronic structure and the Fermi surface. A de Haas–van Alphen (dHvA) effect in thorium was first observed by Thorsen, Joseph, and Valby[1] about two years ago, but these authors experienced considerable difficulty in resolving the various dHvA frequency branches in their impulsive-field experiments. At that time, the crystals available were of relatively poor quality, with resistivity ratios $R_{293°K}/R_{4.2°K}$ less than 100; and techniques for the digital recording and analysis of impulsive-field dHvA data had not been developed. In consequence, Thorsen, Joseph, and Valby were not able to claim a unique interpretation of many of their results. The availability of thorium samples of somewhat higher quality at this laboratory[2] and the current interest in first-principles calculations of the band structure of the actinides[3] have motivated us to reexamine the dHvA effect in thorium.

Our samples were prepared from thorium refined by means of the electrotransport method.[4] $R_{293°K}/R_{4.2°K}$ for a strain-annealed rod from which the crystals were cut was approximately 160 (a disappointingly low figure considering the fact that ratios as high as 1200 have been reported for polycrystalline thorium refined by the same technique).[5] Our crystals were roughly cylindrical in shape with typical dimensions about 1 mm. The samples were studied in a 61-kG superconducting solenoid, the field strength being monitored by the NMR of an Al^{27} specimen in the immediate vicinity of the thorium crystal.[6] The signals were detected inductively through parallel modulation of the main field H by an alternating field of frequency $\nu \sim 40$ Hz and amplitude $\lesssim 150$ G, which could be programmed to vary as H^2. Stark's over-modulation technique[7] was used throughout, with the lock-in amplifier usually tuned to either 2ν or 4ν. The data were recorded digitally, and then analyzed by the filter-periodogram method.[8]

As was also found by Thorsen, Joseph, and Valby,[1] our dHvA frequencies were observed to fall, broadly speaking, into two distinct sets (see Fig. 1); in addition, a new low-frequency branch A was detected. The oscillations in the 11- to 14-MG range are fairly complex, and the important feature of this work is that we have been able to resolve these data into distinct frequency branches. The smooth curves superimposed on the experimental points in Fig. 1 are the frequency variations expected from the Fermi surface predicted by Gupta and Loucks,[3] with the small letters referring to the extremal orbits shown in Fig. 2; the areas $\mathfrak{a}$ of these orbits have been translated into dHvA frequencies using the Onsager relation $F = (\hbar c/2\pi e)\mathfrak{a}$. The Gupta-Loucks model actually gives rise to more frequency branches than we have been able to detect thus far, and for the sake of clarity we have used solid curves in Fig. 1 to indicate those portions of the model branches which are considered to correspond to the available data; the predicted frequency variations are shown as dotted curves elsewhere.

The experimental and theoretical curves which are believed to be related to one another have been labeled with the same letters, capital and lower case, respectively, and these relationships have been established in a fairly unambiguous fashion from symmetry considerations. Thus, beginning with the frequencies around 12 MG, we note for example that the symmetries of the observed branches in the vicinity of the ⟨100⟩ frequency M have an immediate counterpart in the predicted frequency variations for extremal orbits of type m. Likewise, the observed crossing

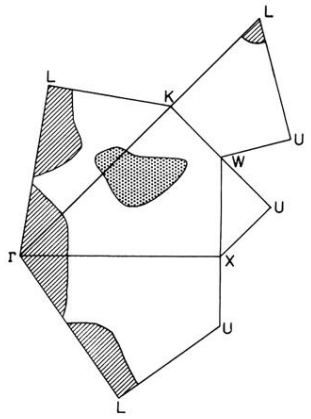

FIG. 3. Intersections of the Fermi surface with the faces of the Brillouin zone, with the holes lined and the electrons dotted.