Observation of Itinerant 5*f* States in Thorium Metal*

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Normal-incidence reflectivity measurements between 0.5 and 6 eV on thorium metal reveal the existence of bandlike (or itinerant) *f* states several electron volts above the Fermi energy. The predictions of relativistic band-structure determinations are in qualitative agreement with experiment. This study provides the first direct observation and characterization of 5*f* electrons in metals as being itinerant in nature and unlike the 4*f* states in the rare earths.

Despite extensive investigations, the nature of the 5*f* states in the actinide metals is not as yet understood. The often-used analogy with the 4*f* electrons of the rare earths would consider them as localized atomiclike states and hence a band description would be inappropriate. However, since the 5*f* atomic orbitals were found to extend further out from the atomic cores than the well-localized 4*f* orbitals, the suggestion was made that the 5*f* states might delocalize into bands. A number of relativistic augmented-plane-wave (RAPW)[1] energy-band calculations[2,3] on the high-temperature (cubic) phases of these metals have indicated that this is indeed the case for the lighter actinides Th–Pu, whereas the heavier actinides behave much like the light rare earths.[4] Unfortunately, the lower-temperature phases of the light actinides are structurally complex, making both the band calculations and interpretations of experimental data for these metals extremely difficult. Thorium, at the beginning of the series, has the fcc structure as its low-temperature phase and thus appears to be an ideal candidate for theoretical and experimental investigations. The availability of high-purity single crystals has permitted accurate de Haas–van Alphen (dHvA) measurements to be made on this (and only this) actinide metal.[5]

The published theoretical studies on Th have followed different paths. Keeton and Loucks[6] used the RAPW method of Loucks with full Slater exchange ($\alpha = 1$) and found energy bands, believed by them to be *s*-*d* bands, which did not correlate well with the dHvA measurements of Thorsen, Joseph, and Valby[5] because (as pointed out by Waber) their 5*f* levels turned out to be in the middle of these bands. To deal with this difficulty (and since it was expected that there would be no occupied 5*f* states in Th), Gupta and Loucks[7] artificially removed the 5*f* bands from their calculations and obtained good agreement with the dHvA measurements. As justification of their procedure, Gupta and Loucks argued, in analogy with the case of the localized 4*f* electrons, that the position in energy of the 5*f* states was very sensitive to the potential and to intra-atomic exchange interactions not included in the band model. By contrast, Freeman and Koelling[2,3] argued that the 5*f* electrons in the lighter actinides are sufficiently delocalized to overlap significantly neighboring atoms and to hybridize strongly with the 6*d* and 7*s* bands. In this case, the *f* electrons have small Coulomb correlation energy (relative to the now large effective band width) and hence must be considered itinerant. Unfortunately, the electronic structure of thorium metal has no occupied states of *f* character so that Fermi-surface data[5] were unable to distinguish between the two theoretical models which we shall refer to as the itinerant model (*f* states included) and the localized model (*f* states removed, the rare-earth analogy).

We here report the first normal-incidence reflectivity measurements on an elemental actinide. These data, together with the theoretical predictions of two models, provide a determination of the electronic structure of thorium metal. We find that the itinerant model correctly predicts the existence of bandlike *f* states 1–5 eV above the Fermi energy. These optical measurements thus provide the first unambiguous experimental observation and characterization of itinerant 5*f*

electrons in metals.

The experimental measurement of $\epsilon_2(\omega)$ was obtained from a Kramers-Kronig inversion of normal-incidence reflectivity data taken between 0.5 and 6 eV at 290°K. The measurements were taken on bulk thorium samples measured at ~3 $\times 10^{-7}$ Torr. To ensure that the sample surface was adequately clean, the following preparation procedure was used: A 99.99%-pure thorium sample was cut into an ingot of dimensions $7.8 \times 3.2 \times 1.2$ mm^3 and was polished (3 μm diamond grit). This sample was then heat treated for 3 h at 1300°C in a vacuum furnace at 5×10^{-6} Torr to remove any residual strain or bcc phase contamination. It was then heavily electropolished in a solution of 4 parts perchloric acid, 4 parts acetic acid, and 1 part water to remove any surface contamination which may have appeared in the heat-treating process. The sample was then sputter etched in a glow discharge at ~50 μm argon pressure for 30 min at 1000 V and was then transferred to the reflectometer without exposure to air. Whereas subsequent exposure to air did not appreciably alter the measured reflectivity, the ion sputtering significantly enhanced the observed structure over that seen with the chemically polished surface. The sputtering introduced some surface roughness, however, so that an overcoating measurement technique[8] was used to compensate for the roughness-induced light loss.

For the Kramers-Kronig inversion, the data were extrapolated to zero and infinite energies using Drude free-electron expressions. Physically reasonable results were obtained by choosing the extrapolation model function parameters in order to satisfy the sum rule

$$n_{\mathrm{eff}}(\omega_0) = (m/2\pi^2 Ne^2)\int_0^{\omega_0} \omega \epsilon_2(\omega)\, d\omega, \qquad (1)$$

where N is the atom density of the solid. This gives the effective number of electrons per atom available for excitation by a photon of energy $\hbar\omega_0$. We obtained $n_{\mathrm{eff}} \simeq 7$ at 100 eV, which we believe to be a reasonable result since the oscillator strength of the four valence electrons and some fraction of the eight outermost core electrons would be exhausted by 100 eV. A variety of model functions were used to test the sensitivity of the inverted optical parameters ϵ_1 and ϵ_2 to the choice of extrapolation. No significant changes in the shape of ϵ_2 were found although the magnitude of ϵ_2 was sensitive to the extrapolation. For our purposes, however, this is not important since we are unable to scale the theoretical calculations quantitatively.

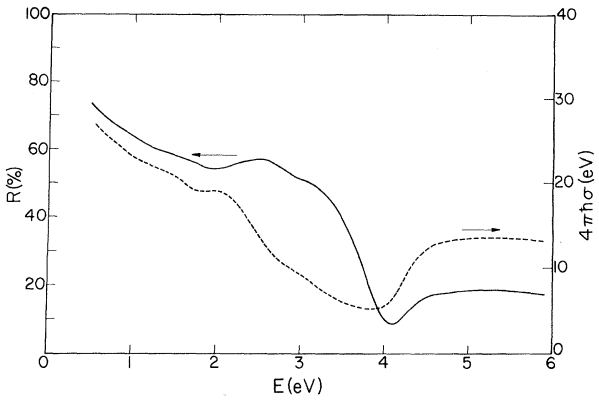

FIG. 1. The reflectivity (solid line) and optical conductivity (dashed line) for thorium. The appropriate scale are indicated by arrows.

Figure 1 shows the reflectivity along with the optical conductivity $4\pi\hbar\sigma(\omega) = \hbar\omega\epsilon_2(\omega)$ obtained from the Kramers-Kronig inversion. The conductivity contains an intraband contribution which cannot be uniquely extracted. However, the superimposed interband features are sufficiently prominent so that meaningful comparisons can be made between theory and experiment. We have made an estimate of the intraband function by assuming the interband absorption was small at the low-energy extreme of the data range and, of course, less than the total $\sigma(\omega)$ at the minimum near 4 eV. The two parameters needed for the free-electron expression

$$\sigma(\omega) = \omega_p^{2}\tau/4\pi(1+\omega^2\tau^2) \qquad (2)$$

were thus estimated to be $\hbar\omega_p = 5.0$ eV and $\tau/\hbar = 0.8$ eV^{-1}. For the subsequent discussion, we have extracted the intraband contributions and show the result as the experimental curve in Fig. 2.

Consider now the predictions of the RAPW calculations. The potential used for both models was constructed by overlapping atomic charge densities created with a d^2s^2 configuration (and in separate calculations with a d^3s^1 configuration). We used the Kohn-Sham-Gaspar exchange approximation (Slater $\rho^{1/3}$ exchange scaled down by $\frac{2}{3}$). In the localized model (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" calcula-

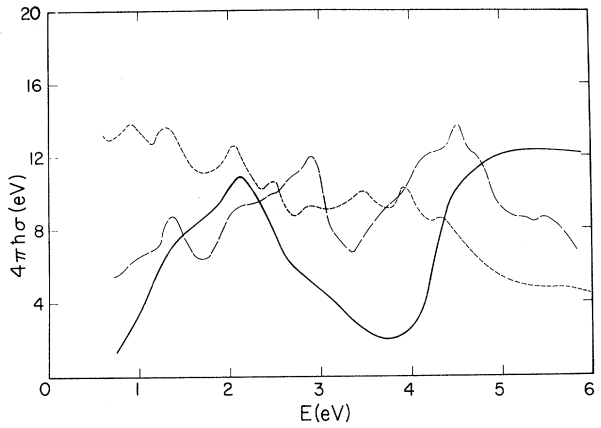

FIG. 2. The experimental interband conductivity (solid line) compared with the results calculated from the itinerant-f (long dash) and localized-f (short dash) models. PSE's (see text) have been used for the itinerant model and joint densities of states have been used for the localized model.

tion differs somewhat from that of Gupta and Loucks[7] who used full Slater exchange 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.

As seen in the experimental curve of Fig. 2, there is a strong interband absorption peak centered at 2.1 eV followed by a strong absorption threshold at approximately 4.2 eV. These two major features must surely provide the important test of any band calculation although additional structure is apparent, including a prominent shoulder at 1.4 eV and a slope change at 2.7 eV. The strong features are most likely due to a large contribution to the joint density of states resulting from transitions between bands which are nearly parallel over an extended region of the Brillouin zone. Thus, for both models, we have calculated the quantity

$$\sigma_{\mathrm{int}}(\omega) = \langle C/\omega \rangle \sum_{n,n'} \int |M_{nn'}(\vec{k}, \omega)|^2 \times \delta(E_n - E_{n'} - \omega)\, d^3k, \qquad (3)$$

where C is an arbitrary constant. We assumed that the $M_{nn'}$ are independent of $\vec{k}$ and band indices—a clearly gross (but popular) approximation that eliminates the possibility of quantitative agreement with experiment. This joint density-of-states approximation is used on the assumption that the structure in σ_{int} results from the energy-conservation requirement with comparatively minor modifications to be expected from the oscillator strengths. The integral of Eq. (3) was determined from RAPW calculations at approximately 220 inequivalent points throughout the Brillouin zone by (1) fitting (using the least-squares method) each band (rms errors of 3 to 10 mRy with sixty symmetrized plane waves), and (2) performing a closed Diophantine[9] integration using 640 000 inequivalent sampling points with these symmetrized-plane-wave fits.

To test the sensitivity of our results to matrix elements, we have (for the itinerant model) included the possibility of the oscillator strengths varying with band index but not with $\vec{k}$. We assigned the relative strengths of transitions between each band pair using a very simple rule. Because we know the parity of the bands at Γ, S, and L, we can determine whether transitions are allowed or forbidden at these points. Thus we weight our "pseudo matrix elements" (PSE's) according to the relative number of allowed transitions at these three points. (Computer programs for calculating these matrix elements with RAPW wave functions are being constructed; the qualitative features of these results are expected to be unchanged.[10]) Comparing these two approximate calculations for the itinerant model, we find the PSE yields a reduced size of the two principal peaks by 20% and a sharpened peak structure (without appreciably moving the positions of the peaks). The enhancement of the double-peak structure represents some improvement in the agreement between theory and experiment over the $|M|^2 = 1$ approximation and indicates the importance of including proper matrix elements in Eq. (3).

In Fig. 2, we compare the calculated σ_{int} with the experimental results. We see that the theoretical calculation which includes the f states in the excitation spectrum yields qualitative agreement with experiment. Essentially no agreement exists between experiment and the localized model which omits the f electrons. In particular, we see that the two major pieces of experimental structure are found in calculation only if the f states are included. We should note that while judiciously placed localized f levels might reproduce some of the features of the optical data, we found that even an f level placed optimally in an *ad hoc* fashion (at $E = 0.73$ Ry) reflected the features of the density of states below E_F but did not produce as good agreement with experiment

as does the itinerant model used here.

We have reported optical-conductivity data which provide an unambiguous first observation of the 5*f* states in an actinide metal. The itinerant model provides distinctly better agreement with experiment than does the localized model. Thus, we conclude that the 5*f* electrons found in the thorium excitation spectrum 1–5 eV above the Fermi energy are itinerant in nature. This result provides strong confirming evidence for the prediction[2,3] that the occupied 5*f* states in the lighter actinide metals are itinerant.

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Precession of Positive Muons in Nickel and Iron

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Polarized μ^+ were stopped in Ni and Fe. The magnetic fields at the site of the muons, the initial polarization, and the depolarization time constant were obtained from 300 to 700°K, i.e., through the Curie temperature of Ni. This experiment demonstrated that precession of muons stopped in ferromagnetic material can be observed and, and it determined what the magnitude of the internal fields are: ≈ 150 G for Ni and 4000 G for Fe.

We implanted polarized positive muons in nickel and iron. The magnetic fields at the sites of the muons (B_μ) were measured by observing the precession of the angular distribution of the decay positrons. The same data yielded the initial polarization (P) of the stopped muons and the time constant (τ) of the slow depolarization. Data were collected as a function of temperature from room temperature to 700°K so that we observed the shift from the ferromagnetic to the paramagnetic state in nickel. This experiment demonstrated for the first time that the precession of muons stopped in ferromagnetic material can be observed, and it further determined what the magnitude and direction of the internal fields are.

That the muon can be a fundamentally important tool for condensed-matter physics has recently begun to be recognized.[1] The work of Schenck and Crowe[2] and Brewer *et al.*[3] has shown that the implanted positive muon behaves very much like a hydrogen nucleus, and that muon studies can provide information about lattice structure and chemical reactions. The present Letter provides new evidence of the usefulness of implanted muons for the study of metals and internal magnetic fields. The behavior of hydrogen in metals is of intrinsic interest as one of the simplest alloy problems.[4] It is also a problem of considerable technological importance.[5] The behavior of the hydrogenlike positive muons in ferromagnetic metals is of additional interest