$q_0=0$, keep only the first-order terms and drop q_0 everywhere else. The result is

$$-(gN_0i\beta q_0/4)\int_0^\infty dZ\ \mathrm{sech}^2[\beta(Z^2+4|\Delta|^2)^{1/2}/4]$$
$$\times(\tfrac{1}{3}Z\tau v_F^2q^2)[(Z^2+4|\Delta|^2)^{1/2}(Z^2+\tfrac{1}{9}v_F^4q^4\tau^2)]^{-1}\delta\Delta^\dagger.$$

We consider the case $v_F^2q^2\tau/3\gg 2\Delta$. Then we may drop $|\Delta|^2$ everywhere and pass to the limit of strong scattering so that the τ-dependent term may be replaced by $\frac{1}{2}\pi\delta(Z)$. The final result is the same as in the pure case:

$$-(gN_0i\pi\beta q_0/8)\delta\Delta^\dagger.$$

The approximations we have used to obtain this result are summarized as follows:

$$ql\ll 1,$$
$$T\approx T_c,$$
$$l/\xi_0\approx kT_c\tau\ll 1,$$
$$\Delta\ll v_F^2q^2\tau\ll kT_c.$$

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Superconductivity of Thorium and Uranium*

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The low-temperature susceptibility and specific heat of thorium and uranium have been measured. It is found that thorium becomes a superconductor at $T_c=(1.374\pm0.001)°K$, and has a value of $C_{es}(T_c)/\gamma T_c=2.42$, in good agreement with BCS theory. (Here C_{es} is the superconducting electronic specific heat, and γ is the temperature coefficient of the normal electronic specific heat.) The γ and Θ_D for thorium were found to be (4.31 ± 0.05) mJ/mole deg^2 and $(163.3\pm0.7)°K$, respectively. Both uranium samples appeared to undergo superconducting transitions when observed magnetically, yet both exhibited only normal-state behavior in their specific heat. Hence it seems likely that the apparent superconductivity of alpha uranium is not characteristic of the bulk metal. The γ and Θ_D of the purer uranium sample were found to be (10.03 ± 0.02) mJ/mole deg^2 and $(207\pm1)°K$, respectively.

INTRODUCTION

THERE have been several investigations of superconductivity in the actinide metals thorium[1,2] and α uranium.[2–5] According to magnetic measurements, both metals become superconducting below 1.5°K, but whereas thorium shows a narrow transition at a temperature (~1.37°K) which varies little among samples, α uranium shows surprisingly broad transitions at temperatures which vary considerably from sample to sample, even in high-purity material. The transition temperature of thorium, like that of most superconductors, is depressed by the application of pressure,[6] whereas that of α uranium rises dramatically, 10 kbar being sufficient to raise it above 2°K.[7] Another sur-

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[1] R. A. Hein and N. M. Wolcott, Phil. Mag. **3**, 591 (1958).
[2] R. D. Fowler *et al.*, Phys. Rev. Letters **15**, 860 (1965).
[3] R. A. Hein, W. E. Henry, and N. M. Wolcott, Phys. Rev. **107**, 1517 (1957).
[4] B. B. Goodman and D. Schoenberg, Nature **165**, 442 (1950).
[5] J. E. Kilpatrick, E. F. Hammel, and D. Mapother, Phys. Rev. **97**, 1634 (1955).
[6] J. L. Olsen, E. Bucher, M. Levy, J. Muller, E. Corenzwit, and T. Geballe, Rev. Mod. Phys. **36**, 168 (1964).
[7] T. F. Smith and W. E. Gardner, Phys. Rev. **140**, A1620 (1965).

TABLE I. Impurity content of samples, parts per million by weight. All impurities in thorium, other than those listed, were less than five ppm by weight. Uranium sample *B* was not tested for C, N, or O content. Three dots means the element was not detected in the analysis.

Element	Thorium	Uranium *A*	Uranium *B*	Element	Thorium	Uranium *A*	Uranium B
C	20	15		K		<50	<1
N	10	<10		Li		<1	<0.5
O	200	16		Mg		2	2
Ag		<1	0.2	Mn		<1	7
Al		<5	5	Mo		<20	···
As		<10	···	Na		<10	1
B		<0.1	<0.2	Ni		<5	28
Be		<0.5	···	P		<50	···
Bi		<1	<1	Pb		<1	1
Ca		<20	<2	Sb		<1	···
Co		<5	···	Si		15	85
Cr		<1	5	Sn		<5	···
Cu		<1	5	Ti		<50	···
Fe	20	<2	24	Zn		<50	···

prising feature in the superconducting behavior of α uranium is the fact that a sample studied by one of the authors failed to show any anomaly in its specific heat,[8] although such anomalies have been observed recently in impurity-stabilized β uranium alloys.[9] In view of this contrast in the superconducting behavior of thorium and α uranium, we decided to study systematically the magnetic and thermal behavior of both materials.

THORIUM

The sample used was an arc melted ingot of van Arkel material, supplied by the Metallurgy Division, Atomic Energy Research Establishment. The principal impurities are listed in Table I. It was of cylindrical shape with a length of 4 cm and a mean diameter of 8 mm, weighing 28.2 g. Its specific heat was measured between 1 and 4°K in a cryostat incorporating a mechanical heat switch of standard design. Measurements were made in the normal state with the help of a superconducting solenoid in which the sample was centered. At the end of the experiment the carbon thermometer attached to the specimen was calibrated in exchange gas against a He^3 vapor-pressure thermometer below 1.6°K, and against He^4 vapor pressures at higher temperatures, with an estimated accuracy of ± 0.7 mdeg.

The radioactivity of the specimen caused its temperature to rise slowly when it was thermally isolated, the heating rate being about 200 erg/min. Figure 1 shows some typical temperature-time plots under self-heating alone. In zero magnetic field the curves showed a pronounced kink at 1.374°K, and by comparing two passes the transition temperature could be located with an accuracy of ± 1.5 mdeg. In the presence of a magnetic field the second-order transition becomes first order, and a thermal arrest is observed. The temperature is not entirely stationary during the transition, partly because the geometry of the field changes as it penetrates the specimen, and partly because the field of the superconducting magnet was not entirely uniform, being 8% smaller at the ends of the specimen than at its center. However, the temperature at point *A*, where the specimen emerges entirely into the normal state, should be the transition temperature corresponding to the field at the ends of the specimen, so that one is able to estimate the initial slope of the critical field. By comparing the heating curves in two different fields with that in zero field we derive a mean value

$$(-dH_c/dT)_{T=T_c}=196\pm 5 \text{ G/deg}. \quad (1)$$

This value agrees quite well with the more careful determination by Hein and Wolcott[1] (190 G/deg). Our value for T_c is also in agreement with theirs (1.37°K).

Figure 2 shows the specific-heat data obtained by discontinuous heating in the usual way. The points in the normal state extend to somewhat lower temperatures than those in the superconducting state, because the specimen could be cooled by adiabatic magnetization: if the superconducting specimen were isolated at 1°K

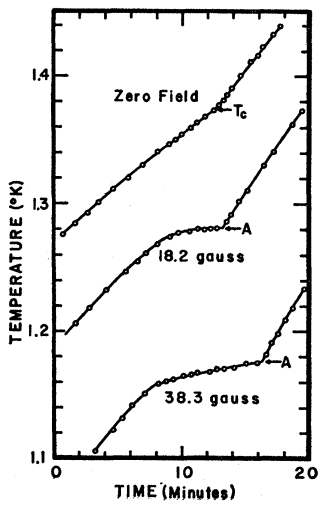

FIG. 1. Self-heating curves of thorium. The field values given in the figure are those at the ends of the sample.

[8] C. W. Dempesy, J. E. Gordon, and R. H. Romer, Phys. Rev. Letters **11**, 547 (1963).
[9] B. T. Matthias *et al.*, Science **151**, 985 (1966).

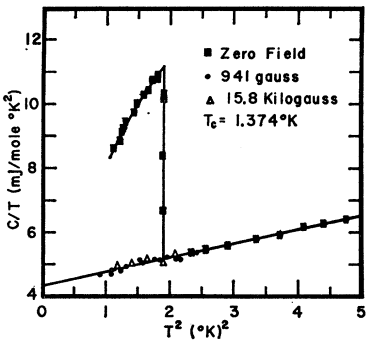

FIG. 2. Specific heat of thorium. The straight line corresponds to the equation

$C=4.31T+1.944\times10^6(T/163.3)^3$ mJ/mole deg.

it cooled below 0.8°K when driven into the normal state. By including data between 2 and 4°K (not shown in the figure) one derives the following values for the electronic coefficient and the Debye temperature: $\gamma=(4.31\pm0.05)$ mJ/mole deg^2, and $\Theta_D=(163.3\pm0.7)$°K. The uncertainties listed include both random and estimated systematic errors.

These values agree only moderately well with those of Smith and Wolcott[10] (4.70 mJ/mole deg^2, 170°K). However, these authors used an exchange-gas technique which is less reliable than ours in principle.

In the absence of a magnetic field the specific heat shows a discontinuity of 8.4 mJ/mole deg at T_c. From this result and the Rutgers equation, one would predict a value of 195 G/deg for $(-dH_c/dT)_{T_c}$ in agreement with the value obtained from Fig. 1. The value of $C_{es}(T_c)/\gamma T_c$ is found to be 2.42, in excellent agreement with the value 2.43 predicted by the BCS theory.[11]

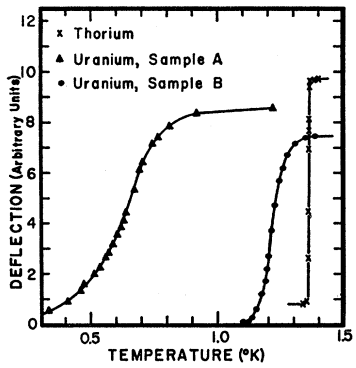

FIG. 3. Superconducting transitions of thorium and uranium. A ballistic galvanometer was used as the detector for the thorium sample and the high-purity uranium (sample *A*). A 14-cps ac mutual inductance bridge was employed as the detector for sample *B*. The vertical scale of the graph indicates detector response and is in arbitrary units. The low-temperature end of each curve corresponds to 100% flux exclusion from the sample (see text).

[10] P. L. Smith and N. M. Wolcott, in *Conférence de Pyysique des Basses Témperatures* (Paris, 1955) [Suppl. Bull. Inst. Intern. Froid, Annexe 1955-3, 283 (1955)].

[11] J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 170.

In addition to the specific-heat data, the magnetic susceptibility of the sample was measured by surrounding it with a closely fitting coil and by recording the ballistic throw on reversing an external field of 1.8 G. Figure 3 shows a narrow transition which extends from 1.365 to 1.355°K. The upper temperature agrees with the transition temperature at 1.8 G calculated from Eq. (1), and the lower temperature for the remainder of the transition can again be explained by the inhomogeneous penetration of the magnetic field.

Hence all our results indicate that thorium is a surprisingly ideal superconductor. The magnetization curves of Hein and Wolcott[1] also indicate that, like most pure metals, it has type-I properties. These authors show that the critical field curve deviates in a negative sense from a parabolic law, so that thorium should conform to the weak-coupling approximation in the BCS theory.[11]

URANIUM

Two samples were used in these measurements. The impurity content is listed in Table I. One specimen (denoted sample *A*) was a high-purity sample obtained from Argonne National Laboratory. It was a cylinder of 9.6-mm radius and 30-mm length, and had a mass of 162.5 g. The specific heat of this sample was studied both in the as-received condition and after a 12-h anneal in the alpha phase at 500°C. All magnetic measurements on this sample were made after the anneal. Some of the measurements of the pressure dependence of T_c for uranium which were reported by Smith and Gardner[7] were made on specimens cut from this sample. The electrical resistivity of specimens cut from this sample was found to be ~1 $\mu\Omega$ cm at 4°K and ρ_{300}/ρ_4 was found to be ~28.

The second uranium sample (denoted *B*) was an "off the shelf" specimen borrowed from Brookhaven National Laboratory. It was a 69.9 g cylinder of 5.6-mm radius and 38-mm length. All measurements on sample *B* were obtained with the sample in the as-received condition. The electrical resistivity of this specimen at 4°K was found to be ~2.5 $\mu\Omega$ cm and ρ_{300}/ρ_4 was found to be ~16.

Magnetic Measurements

The superconducting transistions for the two samples are shown in Fig. 3. It will be noted that the transition associated with the higher purity, annealed sample *A* occurs at a lower temperature and is somewhat broader than that for specimen *B*. However, in view of the wide variations in transition temperatures and widths observed in uranium,[3–5] it would be unwarranted to draw conclusions concerning the effects of heat treatment or impurity level until a systematic study has been made.

The measurements on sample *A* were made in a He^3 cryostat. The specimen was surrounded by two closely fitting coils and ballistic determinations were made by reversing a primary field of slightly less than 1 G. The

coil used in this experiment was not calibrated, but from geometrical considerations it is estimated that the results shown in Fig. 3 correspond to 100% flux exclusion from the volume of the sample.

Both ballistic and ac measurements were made on sample B. As early measurements indicated essentially identical results, the final measurements were made using a 14-cps mutual-inductance bridge in which the measuring field was 0.2 G. In this apparatus the measuring coils in the Dewar consisted of two sets of primary and secondary coils wound so that the mutual inductance of the combination was essentially zero when there was no sample in either set. The coils were calibrated using a high-purity tin sample identical in size and shape to the uranium sample. The change in mutual inductance of the system when the superconducting uranium sample was pulled from one pair of coils to the other was the same (to within 1%) as the change resulting when the superconducting tin sample was moved. We therefore conclude that the measuring field was excluded from the entire volume of the uranium sample. It should be pointed out that when the sample was left inside one pair of coils, the change in mutual inductance when the sample became superconducting was greater for the uranium than for the tin. This effect arises because in the normal state much of the volume of the high conductivity tin sample is already shielded by diamagnetic eddy currents from the field of our 14-cps measuring current. This shielding effect is much smaller for the relatively impure uranium; from measurements at 4.2°K we infer penetration depths for the normal metals of 2.1 cm for the uranium and only 0.025 cm for the tin. It is clear, as was recognized by Shoenberg[12] many years ago, that caution must be observed in calibrating an ac device if spurious claims concerning "100%" superconducting transitions are to be avoided.

Susceptibility measurements in steady magnetic fields were also made on sample B between 1.08 and 1.35°K. It was found that the field necessary to destroy superconductivity in the sample at 1.08°K was ~200 G. Magnetization measurements were also made on this sample at 1.08°K but even in fields as small as 1 G extreme hysteresis was observed. Since this sample was not one of extremely high purity, these experiments were not extended. Attempts were made to observe a Meissner effect in sample B, but no detectable flux expulsion was observed when the sample was cooled in the presence of a magnetic field of 12 G. Similarly, no flux change through the volume of the measuring coil was observed when the sample was warmed above the transition temperature in the presence of this field. These results on B lend support to the view that the superconductivity observed in uranium is due to some sort of filamentary structure rather than to the bulk sample.

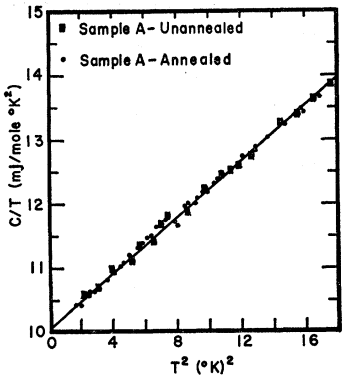

FIG. 4. Specific heat of uranium (sample A) between 1 and 4°K. The straight line corresponds to the equation

$$C = 10.03T + 1.944 \times 10^6 (T/207)^3 \text{ mJ/mole deg.}$$

Specific-Heat Measurements

The specific-heat measurements on sample A between 1 and 4°K which are shown in Fig. 4 were made by the same techniques used for thorium. Measurements on this high-purity uranium sample were made both before and after the anneal. The results indicate that the sample's heat capacity was not affected by the annealing. The γ and θ_D values were found to be (10.03 ± 0.02) mJ/mole deg^2 and (207 ± 1)°K, respectively. The uncertainties listed correspond to the standard deviations in the constants obtained from a least-squares fit of the experimental results. The γ value is considerably lower than the values of 10.9 and 10.6 mJ/mole deg^2 found by Smith and Wolcott[10] and Goodman *et al.*[13] However, in view of the relatively high purity of sample A, this somewhat lower value is not surprising.

The specific heat of sample A both before and after the anneal was also measured between 0.64 and 2°K in a He^3 cryostat using as a thermometer a germanium resistor which had been calibrated against He^3 vapor pressures. These results, shown in Fig. 5, gave a γ of (9.98 ± 0.07) mJ/mole deg^2 and a Θ_D of (209 ± 20)°K. These values are in good agreement with the higher temperature results. Hence we must infer from these specific-heat results that the bulk of the sample re-

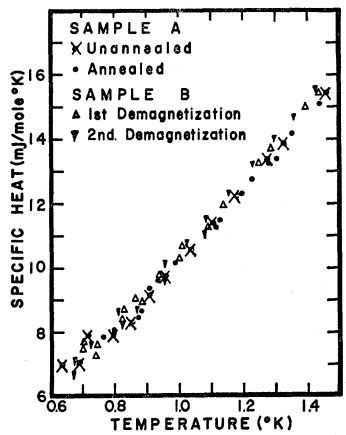

FIG. 5. Specific heat of uranium between 0.6 and 1.5°K. The measurements on sample A were made in a He^3 cryostat, those on sample B in an adiabatic demagnetization cryostat.

[12] D. Shoenberg, Proc. Cambridge Phil. Soc. 33, 559 (1937).

[13] B. B. Goodman *et al.*, Compt. Rend. 250, 542 (1960).

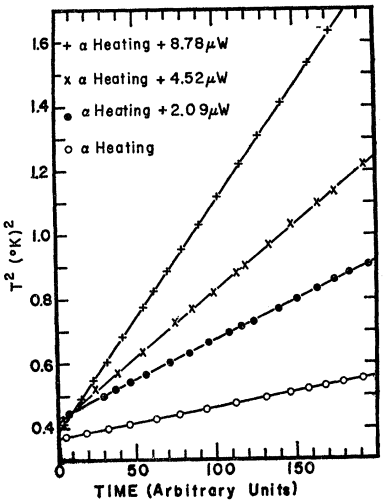

FIG. 6. Variation with time of the square of the temperature of uranium sample B. 100 arbitrary time units on the graph correspond to 118 sec.

mained in the normal state at temperatures as low as 0.65°K, even though the magnetic measurements on this same sample indicated flux exclusion from a significant volume of the sample at this temperature.

The specific heat of sample B was measured in an adiabatic demagnetization cryostat which utilized iron ammonium alum as the cooling salt. The thermometer used in these experiments was a 470-Ω Speer resistor. Temperatures between 0.6 and 1.4°K were obtained from the equation $T=A\ \ln R/(\ln\ R-B)^2$, where the constants A and B were determined by calibrating the resistor against He^4 vapor pressures above 1.4°K.

The magnet used in the demagnetization experiments was a superconducting end-corrected solenoid 4.5 cm in diam and 13 cm long. When the current in the solenoid was reduced from its maximum value to zero, the residual field at the center of the solenoid was found to be less than 20 G. However, in order to ensure that the residual field at the sample position (~13 cm from the center of the solenoid) should be as small as possible during at least part of the experiment, two separate demagnetizations of the salt were made. After the first, a small reverse current was applied to the magnet so that the residual field outside the Dewars was less than the earth's field; the uranium was then cooled through the superconducting transition to the salt temperature using a mechanical heat switch. In the second demagnetization the magnet current was reduced directly to zero, the sample again being subsequently cooled from the normal state using the heat switch. Under these circumstances the maximum value of the residual external field was 3 G. No difference in the specific-heat results obtained under these two sets of circumstances was observed.

The results on sample B are shown in Fig. 5. A least-squares fit to the experimental data gave values for γ and Θ_D of (10.12±0.05) mJ/mole deg² and (182±6)°K, respectively. The somewhat low value for Θ_D can be attributed to uncertain addenda corrections. Because of this uncertainty and because sample B was less pure than A, the results obtained above 1°K for sample A must be regarded as yielding the more reliable values of γ and Θ_D for high-purity uranium.

It is clear from Fig. 5 that the results on B show no hint of the kind of specific-heat anomaly usually associated with a superconducting transition. While the results on A go only to the middle of the transition, those on B go to temperatures corresponding to $T\sim\frac{1}{2}T_c$, yet in neither case do the data give evidence of a specific-heat anomaly.

However, in order to confirm the absence of a bulk superconducting transition, a second method of making specific-heat determinations was employed. The sample was cooled down to ~0.6°K by connecting it to the paramagnetic salt via the mechanical switch. The switch was then opened and the warm-up of the sample was observed. In one case the warm-up was due solely to the self-heating resulting from the alpha activity of the sample. In other cases the warm-up resulted from the combined effect of the α heating and heater inputs varying from 2.1 to 8.8 μW. If uranium is in the normal state below 1°K, then its specific heat varies essentially linearly with T. In this case T^2 will vary linearly with time, provided that the total heat input to the sample is constant. A graph of the results is shown in Fig. 6. From a comparison of the slopes of these curves one can obtain moderately good values for γ and for the α heating of the sample. These results, when corrected for the addenda heat capacity and for the small T^3 term contribution to the specific heat, yielded a value for γ of 10.6 mJ/mole deg² and of 13.5 erg/sec for the α heating. The latter value is in agreement with the value of ~13 erg/sec calculated from the measured activity of natural uranium.[14] More importantly, these "drift" results clearly show the absence of any anomalous departure from a T dependence of the specific heat below 1.35°K in a sample which, on the basis of magnetic susceptibility measurements, appears to undergo a complete superconducting transition between 1.10 and 1.35°K.

Discussion

It is clear from these results that uranium cannot be regarded as a typical bulk superconductor. The magnetic behavior of our samples, and in particular the highly irreversible character of the magnetization, strongly suggest the existence of a multiply connected superconducting network in α uranium at low temperatures. Such a network, distributed throughout a sample which is predominantly normal-state material, would be capable of screening the bulk of the sample from a magnetic field and yet would not significantly contribute to the heat capacity.

[14] E. H. Fleming, A. Ghiorso, and B. B. Cunningham, Phys. Rev. 88, 642 (1952).

It seems likely to us that this network is composed of regions which have been strained by the highly anisotropic volume changes of the grains in a polycrystalline sample cooled to helium temperatures. Such a model is metallurgically feasible and is compatible with (1) the variation of T_c from sample to sample, (2) the broad width of the observed transitions, (3) the strong pressure dependence of T_c, and (4) the specific-heat anomaly in uranium under pressure which has recently been observed by Phillips *et al.*[15] Such a network of strained regions in polycrystalline uranium has been postulated by Geballe *et al.*,[16] but these authors suggest the coexistence of this network with a second filamentary structure composed of β or γ phase material. Howlett,[17] however, has pointed out that metallurigical evidence makes it unlikely that such β or γ phases can exist in a high-purity uranium sample. Since, as Geballe *et al.* recognize, such phases would not show the observed pressure dependence of T_c, and since, in our opinion, the evidence cited by these authors in support of the existence of such β or γ phases can equally well be regarded as support for a network of strained material, it appears to us that the latter network alone is sufficient to explain the experimental results reported so far.

However, the details as to why strains encourage superconductivity in uranium are not clear. Geballe *et al.*[16] suggest that the anomalous thermal expansion below 40°K [18] is evidence for the transfer of electrons from the $6d$ band to what are, essentially, localized $5f$ states. They argue that the presence of these states inhibits superconductivity. When a sample is subject to pressure, the number of $5f$ electrons is reduced and T_c is accordingly raised. In terms of such a model, however, the observed absence of a temperature-dependent magnetic susceptibility[19] is difficult to explain.

Smith and Gardner[7] also argue that the superconductivity of uranium is intimately associated with the existence of $5f$ electrons. Hamilton and Jensen[20] had earlier proposed that uranium's superconducting properties could result from the existence of a low-lying virtual f level. Smith and Gardner, however, postulate the existence of a $5f$ band (sufficiently broad to explain the absence of a temperature-dependent susceptibility) and regard the occurrence of superconductivity in uranium as arising from the admixture of $5f$ wave functions at the Fermi surface. Such an admixture, in their view, is increased by the application of pressure.

Thus, there appears to be agreement that the peculiar superconducting properties of uranium are dependent upon the existence of occupied $5f$ states, though the role played by these states remains controversial. The absence of a strong pressure dependence in T_c for throrium supports the view that in this metal, states with $5f$ character lie well above the Fermi surface.[21,22]

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[15] N. E. Phillips, J. C. Ho, and T. F. Smith, to be presented at the 10th International Low Temperature Conference, Moscow, 1966.
[16] T. H. Geballe *et al.*, Science **152**, 755 (1956).
[17] B. W. Howlett (to be published).
[18] C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).
[19] W. E. Gardner (private communication).
[20] D. C. Hamilton and M. A. Jensen, Phys. Rev. Letters **11**, 205 (1963).
[21] G. W. Lehmann, Phys. Rev. **116**, 846 (1959).
[22] S. C. Keeton and T. L. Loucks, Phys. Rev. **146**, 429 (1966).