Effect of Nonmagnetic Localized States on the Superconducting Critical-Field Curves of *Th*U Alloys

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(Received 17 April 1973)

Superconducting critical-field curves for *Th*U alloys obey the predictions of the Bardeen-Cooper-Schrieffer theory to an accuracy of about 2% and show no evidence for the lifetime broadening of Cooper pairs. This implies that the basic interaction by which superconductivity is destroyed in this system preserves time-reversal symmetry. Nonmagnetic resonant states can be extremely detrimental to superconductivity even though they show no spin-flip breaking of Cooper pairs.

INTRODUCTION

There is strong evidence that uranium impurities in a thorium host exhibit an Anderson-Friedel[1,2]-type nonmagnetic resonant state at the Fermi level and indeed the localized-spin-fluctuation theory[3] (LSF) seems to apply for this system rather well. Maple and co-workers[4] first showed that the low-temperature electrical resistivity ρ of *Th*U obeyed the LSF relation $\rho \sim (1 - T^2/T_0^2)$, where T_0 was about 100 K and from susceptibility measurements they also found that the effective moment for the uranium impurity decreases rapidly below the free-ion value for temperatures about 100 K and appears to approach zero at $T = 0$. In addition, the concentration n dependence of the superconducting transition temperature T_c has positive curvature with approximately the shape predicted by Kaiser[5] for nonmagnetic resonant states. This positive curvature is in direct contrast to the negative curvature expected if the impurity atom has a well-defined temperature-independent localized moment as described by Abrikosov and Gor'kov (AG).[6] Indeed, on the basis of measurements of the concentration dependence of T_c for several different alloy systems, *Th*Ce, *Th*U, and *Al*Mn, Huber and Maple[7] suggested that one could determine the magnetic behavior of the impurity from the shape of the T_c-vs-n curve. In broad outline, they suggest that positive curvature of T_c vs n implies local-moment behavior and negative curvature implies the absence of a well-defined local moment.

There are several different theoretical models which might explain the observed depression of T_c with n. Bennemann[8] suggested that the spin-scattering rate τ_s^{-1} of Cooper pairs might decrease as the temperature decreases because the probability of a localized spin fluctuation decreases as T diminishes. Keller and Fulde[9] have suggested that τ_s^{-1} might decrease because the population of crystal-field levels decreased with lower temperatures. Müller-Hartmann and Zittartz[10] and Maki[11] have suggested that Kondo scattering might give rise to both positive and negative curvature T_c-vs-n curves depending on the ratio of T_c to the Kondo temperature T_K. All of these theories[8-11] predict that T_c is depressed by a temperature-dependent pair-breaking mechanism. Kaiser,[5] on the other hand, uses a Hamiltonian which is time-reversal invariant and predicts the observed T_c-vs-n curves by simply diminishing the strength of the effective BCS attractive interaction. In this theory the impurity atoms destroy superconductivity through an enhancement of the Coulomb repulsion by the Anderson mechanism rather than destroying superconductivity through a spin-flip or pair-breaking process.

Critical-field-curve measurements provide means to distinguish whether the impurity destroys superconductivity by the Coulomb repulsion mechanism or by the spin-flip mechanism. If the Coulomb repulsion effect dominates, the critical-field curves will follow the Bardeen-Cooper-Schrieffer (BCS) theory with a modified T_c. If the spin-flip effect dominates, the critical-field curves will deviate from BCS[12] toward the AG[6] prediction or in a way described by Maki.[11] Hence a detailed study of the superconducting critical-field curves for *Th*U alloys has been undertaken to determine whether the uranium impurities destroy superconductivity by weakening the pairing interaction[5] or by lifetime broadening.[6,8-11] Smith[13] has made a similar study for *Al*Mn alloys which have a characteristic spin-fluctuation temperature of about 500 K and found essentially BCS behavior. The *Th*U alloys studied here have a spin-fluctuation temperature five times smaller so any lifetime broadening effects would be much more pronounced in this system.

EXPERIMENTAL

Sample Preparation

A master alloy of Th–1.88% U (all concentrations will be quoted in atomic percent) was prepared by a conventional arc-melting technique which utilized

an argon atmosphere, a water-cooled copper hearth, and a tungsten tip. Portions of the master alloy were then diluted with pure Th to give the desired U concentration. Each sample was arc melted four times to provide good homogeneity. The weight change indicated that a negligible amount of U was lost on melting. The arc-melted button was then swaged into a cylindrical shape 3.3-cm long by 0.25-cm diameter, electropolished in a perchloric acid and methanol solution, sealed in a Ta crucible, and annealed above the recrystallization temperature, 800 °C, for 1 h to relieve strain. With this heat treatment the samples showed transitions which were broader than expected for the demagnetizing factor and the hysteresis was usually about (5–7)% of the critical field H_c. Therefore the samples were wrapped in Th foil, sealed in a Ta crucible and annealed again at 1200 °C for 7 days. Solid solubility of U in Th is greater than 1.5 at.% at these temperatures so this anneal has a homogenizing effect. This anneal reduced the transition widths to the value expected for the demagnetizing factor and markedly reduced the hysteresis in five of the samples. Unfortunately two other samples, the 0.050- and 0.075-at.%-U, still showed broad transitions and about 7% hysteresis after the 1200 °C anneal. We do not understand why these samples did not improve as a result of the anneal whereas the other samples improved substantially. Critical-field curves for the 0.050- and 0.075-at.%-U samples agree well with the samples but the error bars were so large that they are not reported here.

Apparatus

The apparatus used in these experiments was essentially the same as that reported earlier by Decker and Finnemore[14] (DF) so a brief discussion of a few of the details will suffice here. A standard He^3 refrigerator was used to provide temperatures which were steady to a precision of 0.0001 over the range 1.4–0.3 K during the $\frac{1}{2}$-h period needed to make the magnetization measurements. Temperatures were measured with a germanium resistance thermometer (GR 928) which had previously been calibrated using the vapor pressure of He^4 and the susceptibility of cerium magnesium nitrate. Magnetic fields were provided by a sixth-order Garrett solenoid which had been calibrated against the nuclear magnetic resonance of protons in water. The superconducting-to-normal transitions were detected by a field-stepping technique similar to that developed by Cochran, Mapother, and Mould[15] and the superconducting transition temperatures for some of the samples were determined by a standard 32-Hz ratio-transformer bridge.

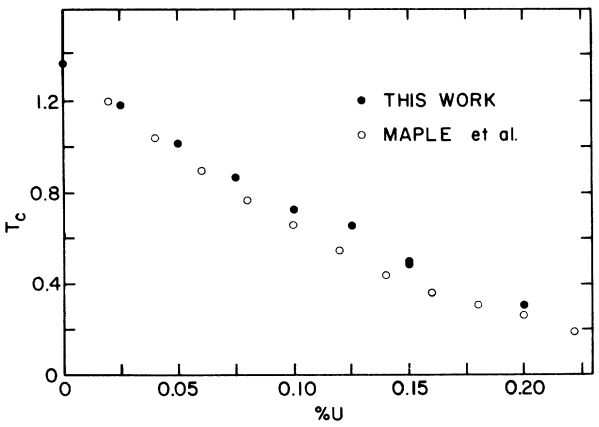

FIG. 1. Concentration dependence of T_c. The systematic difference between this work and the results of Maple *et al.* (Ref. 4) may arise because different annealing procedures were used.

RESULTS AND DISCUSSION

The superconducting-to-normal transitions in zero applied field as determined by an ac susceptibility technique were about 0.003 K wide indicating that the samples are rather homogeneous. Values of the superconducting transition temperature T_c were determined either from the midpoint of the ac susceptibility transition or by an extrapolation of the critical-field curve to $H=0$ with the relation $H_c = A + BT^2$. In cases where both methods were used the results agree to an accuracy of 0.002 K. The dependence of T_c on n is in rather good agreement with previous work by Maple *et al.*[4] (Fig. 1), but there are systematic differences which may arise because the samples reported here were annealed at 1200 °C. On a $\ln T_c/T_{cp}$-vs-n plot (T_{cp} is the transition temperature of pure Th) these data are more nearly linear than the previous data.[4]

Hysteresis in the superconducting transition is the primary factor limiting the accuracy of these critical-field measurements so a fairly extensive study of this phenomenon was made. Annealing affects the hysteresis strongly as illustrated in Fig. 2. After the samples had been annealed at 800 °C for 1 h to relieve strain, the transitions were much broader than expected from the demagnetizing factor and the hysteresis tended to be about (6–7)% of H_c. After the homogenizing anneal at 1200 °C for 7 days, the transitions for four samples (the 0.50, 0.100, 0.125, and the 0.150% U) sharpened to the expected demagnetizing slope and the hysteresis decreased by about a factor of 5. As shown on Fig. 2, the anneal tended to collapse both sides of the hysteresis loop toward the center so we have defined H_c as the midpoint between the field-increasing and field-decreasing transitions. In broad outline the hysteretic behavior of these *Th*U alloys is the same as for the *Th*Gd alloys[14]

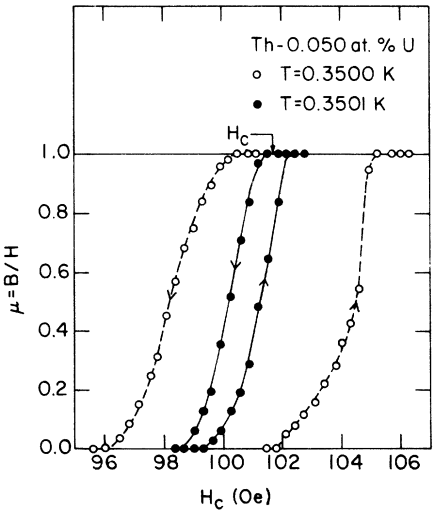

FIG. 2. Hysteresis in the effective premeability μ for increasing and decreasing fields.

reported earlier.

The magnitude of the hysteresis for those samples which were annealed at 1200 °C generally speaking was less than 1% but some other samples did not follow this pattern. The Th 0.05-, Th 0.102-, Th 0.125-, and the Th 0.150-at.% samples each had a maximum hysteresis of 1% but the Th 0.030-at.%-U sample had a hysteresis of 3% at the lowest temperatures and two other samples not reported in detail here (0.050% U and 0.075% U) showed 7% hysteresis at the lowest temperatures. For some reason, the 1200 °C anneal did not improve these latter two samples significantly.

Critical-field data for these *Th*U alloys, shown on Fig. 3, follow the BCS theory[12] much more closely than they follow the AG theory. In the concentration range explored here the critical field predictions differ by about 10% so the experimental accuracy of about 1% allows one to make a clear distinction between the two theories. Unless otherwise shown, the error bar for each data point on Fig. 3 is smaller than the size of the dots. An important point to realize in comparing the data with theory is that both the BCS and the AG theoretical curves are forced to fit the experimental data at one point only, T_c. Once the properties of pure Th and the ratio of T_c/T_{cp} are known, the AG critical-field curve can be calculated from the work of Skalski *et al.*[16] Similarly, the BCS curve can be calculated from the properties of pure Th and T_c/T_{cp} with only small corrections for changes in the anisotropy of the energy gap[17,18] and changes in the density of states[19] with U concentration. For both cases, H_0 and the shape of the curve are determined by the theory. The Th 0.125-at.%-U sample, shown by the open squares in Fig. 3, is a rather high concentration alloy with less than 1% hysteresis so it has been chosen to illustrate the comparison of the data to the theories. Some of the other theoretical curves have been omitted to keep the figure less crowded. The AG theoretical curve lies about 10% below the experimental data and this difference is well outside the experimental accuracy. The BCS curves lie slightly below the experimental data but the difference is scarcely outside the accuracy and could well be caused by inaccurate assessment of the changes in the density of states or the specific-heat coefficient γ.[19]

For a detailed assessment of how well the data obey the BCS theory it is necessary to examine the anisotropy and density-of-states corrections in somewhat more detail. Anderson *et al.*[17] first determined the mean-square anisotropy of the energy gap in Th to be $\langle a^2 \rangle = 0.021$ by measuring the change in T_c with normal-state resistivity ρ as carbon impurities were added. Subsequently, Gubser[20] showed that the anisotropy can be estimated to be $\langle a^2 \rangle = 0.019$ from the slope of the critical field at T_c. These two values are rather close so we have chosen the average, $\langle a^2 \rangle = 0.020$, for our analysis here. The increase in γ with U concentration was taken from the specific-heat work of Luengo *et al.*[19] to be 2.7 mJ/mole K at.% so that $\gamma = [4.31 + 2.7\,n]$ mJ/mole K^2. If these values are inserted into Clem's theory[18] for the critical-field curve of superconductors with anisotropic energy gaps, one obtains the solid line curves of Fig. 3. Fortunately, changes in normal-state resistivity ρ with con-

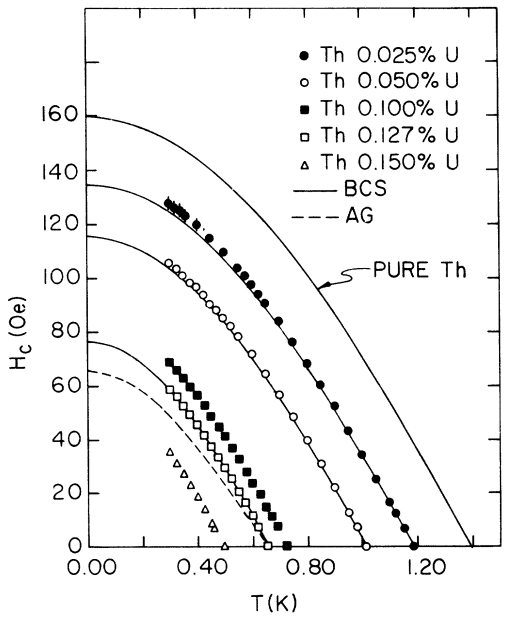

FIG. 3. Critical-field curves for *Th*U alloys. Theoretical curves are forced to fit the data at only one point, T_c.

TABLE I. Properties of *Th*U alloys.

n (at. % U)	T_c (K)	H_0[a] Oe	H_0[b] Oe	γ[a] (mJ/mole K^2)	γ[b] (mJ/mole K^2)	$\frac{\Delta C}{\Delta C_p}$	ρ ($\mu\Omega$ cm)
0[c]	1.360 ±0.002					1.00	
0.025	1.182 ±0.002	136.6 ±1.5	137.1 ±1.5	4.42 ±0.09	4.57 ±0.09	0.879	
0.050	1.014 ±0.002	117.0 ±0.6	117.4 ±0.0	4.41 ±0.04	4.54 ±0.04	0.752	
0.100	0.725 ±0.002	84.5 ±0.2	85.0 ±0.2	4.50 ±0.02	4.64 ±0.02	0.565	
0.125	0.658 ±0.002	76.5 ±0.2	77.0 ±0.2	4.48 ±0.02	4.62 ±0.05	0.514	
0.150	0.495 ±0.002					0.408	
0.200	0.304 ±0.002						
0.075[d]	0.863 ±0.002						

[a] Derived from a simple BCS extrapolation.
[b] Derived from an anisotropy-corrected BCS extrapolation.
[c] Complete critical-field curve not measured; see Ref. 14.
[d] Sample showed large hysteresis so H_0, γ, and ΔC are not reported.

centration are small (see Table I) so that changes in gap anisotropy cause only about 1% change in H_0 over the entire range of n studied. Uncertainty in γ, however, is slightly more serious. We estimate that γ values may be incorrect by as much as (2–3)% and this would cause over 1% uncertainty in theoretical (BCS) value of H_0. The difference between the BCS and AG theories, however, lies well outside these errors.

In principle, one can determine values of H_0 and γ from critical-field data alone by fitting the data below $t = 0.23$ to $H_c^2 = H_0^2 - (4\pi\gamma/v)T^2$. Unfortunately these data do not extend to sufficiently low temperatures to make such a fit. Hence we have used the anisotropy-corrected BCS curves[18,12] to extrapolate the data to $T = 0$ to obtain H_0. For each data point below $t = 0.4$ one can use the anisotropy-corrected BCS theory to give H_c/H_0 and hence calculate H_0 from the measured H_c and T_c/T_{cp}. Values of H_0 derived in this way, shown by Fig. 4, vary by less than 0.3% as a function t indicating that the shape of critical-field curves obeys the theory to this precision. If we then use these H_0 values and the Clem relation,[18]

$$H_0^2 = 8\pi\gamma T_c^2[1 - 2\langle a^2\rangle\chi_H],$$

where χ_H is an anisotropy factor determined from ρ, then we obtain the values of γ listed in Table I and shown on Fig. 5. These critical-field γ values agree fairly well with Wolcott and Hein[21] and with Luengo *et al.*[19] but there may be genuine differences of as much as 3%. The fact that these γ values dif-

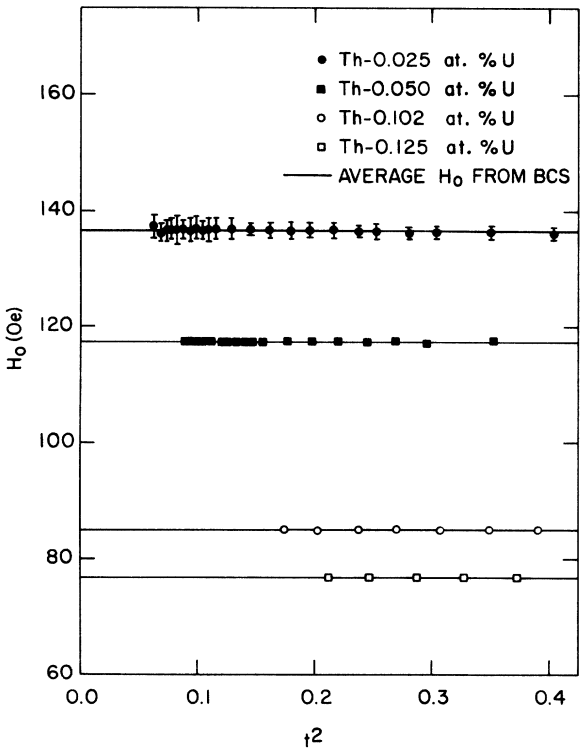

FIG. 4. Temperature dependence of the value of H_0 needed to fit the anisotropy-corrected BCS theory. The constancy of H_0 indicates that the critical-field curves have a BCS shape. The 0.025-at.%-U sample was much larger hysteresis than the other samples. Error bars are smaller than the symbol unless otherwise indicated.

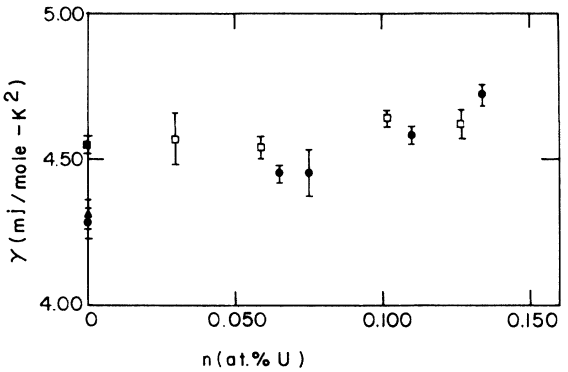

FIG. 5. Concentration dependence of γ. The solid circles are the specific-heat results of Luengo *et al.* (Ref. 19). The open squares were derived from the critical-field curves using the Clem anisotropy correction. The anisotropy correction is about 4% and can make the difference between the uncorrected value of 4.34 (solid triangle) and the corrected value of 4.52 (solid square) for pure Th. The Wolcott-Hein (Ref. 21) value for pure Th is 4.65 mJ/mole K^2.

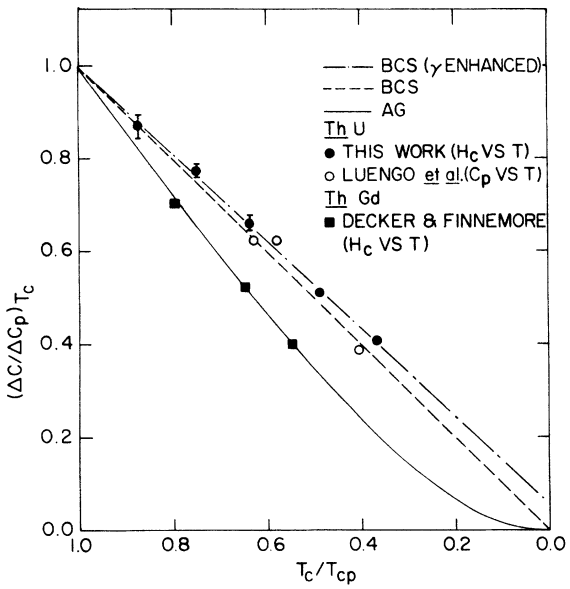

FIG. 6. Jump in specific heat at T_c normalized to the value for pure Th. *Th*U alloys follow the γ and anisotropy-corrected BCS curve very well whereas the *Th*Gd data follow AG very well.

fer from Luengo *et al.*[19] is another way of showing that the critical-field curves of Fig. 3 differ slightly from the anisotropy-corrected BCS theory. Probably the most important point about Fig. 5 is that γ, whether determined by specific heat or by critical-field curves, changes very little. Over the concentration range studied here γ, and hence the density of states, does not vary by more than 8%. Indeed the critical-field γ's, are constant to about 2%. Hence the rapid depression of T_c cannot be explained as a density-of-states effect only. An alternate way to compare the data with the theory which emphasizes the high-temperature data is through the jump in specific heat at T_c, ΔC. If one calculates ΔC from the slope of the critical-field curve at T_c via the Rutger's formula[22] one obtains values shown by the solid circles on Fig. 6. Once again the data lie slightly higher than the simple BCS prediction (dashed line) and very close to the BCS curve which has been corrected for the small increase in density of states (dot-dash line). The AG prediction (solid line), on the other hand, is far below the *Th*U results and is in good agreement with the paramagnetic local-moment case of *Th*Gd[14] (solid squares).

One further way to compare the data with theory is through the ratio of $H_0^2/\gamma T_c^2$. This parameter, of course, emphasizes the relative size of the free-energy difference at $T=0$ to the normal free energy at the transition temperature. As with the previous comparisons, the data (solid circles) agree with the corrected BCS curves but are far from the AG theory. Results for the local-moment case of *Th*Gd are shown by the open circles for comparison.

The central question in this work is to decide which mechanism or combination of mechanisms is responsible for the rapid drop of T_c with uranium concentration. It seems fairly clear from Figs. 3, 6, and 7 that the temperature dependence of the free energy of these alloys follow BCS rather well and that spin scattering of the AG type plays a relatively minor role if any at all. This is consistent with the work of Smith[13] who found that *Al*Mn with a characteristic spin-fluctuation temperature of about 500 K obeys BCS rather than AG. It is significant that *Th*U which has a characteristic temperature five times lower than *Al*Mn still shows no significant effects of lifetime broadening. Fur-

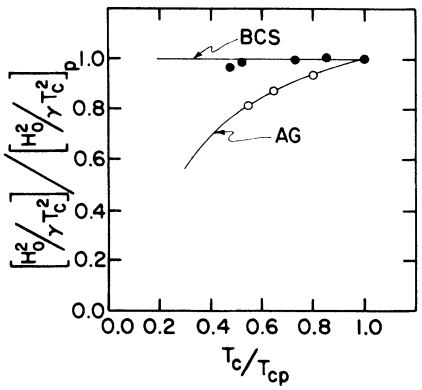

FIG. 7. Ratio of $H_0^2/\gamma T_c^2$ normalized the value for pure Th vs the reduced transition temperature. *Th*U results (solid circles) agree with the corrected BCS curve, *Th*Gd results (open circles) agree with AG.

thermore, from Fig. 5, it is also fairly clear that the average density of states does not change by more than a few percent with these small changes in uranium concentration and indeed it increases rather than decreases with n. Hence it appears that T_c is suppressed by a time-reversal-invariant mechanism which is closely related to the BCS coupling parameter V.

If the transition-temperature data are cast in the form of an effective coupling constant g, as suggested by the work of McMillan[23] and Kaiser,[5]

$$T_c/(\Theta_D/1.45)e^{-1/g},$$

then the measurements indicate that g decreases approximately linearly with uranium concentration as shown in Fig. 8. Within simple BCS theory, $g=N(0)V$, so one would expect a linear decrease in V of about 25% in the concentration range explored. Within the Kaiser theory[5] the coupling constant of the alloy, g, is depressed by a Coulomb repulsion associated with the mixing of the Th-conduction-electron states with a Friedel-Anderson-type resonant state at the U site. In the theory g is related to the value of g for the pure metal, g_p, by the relation

$$g=(1-cd)/(1+c)g_p,$$

where c is the percentage change in the density of states and d is the ratio of the impurity Coulomb repulsion to the pure-metal coupling constant, $d=N_f(0)U_{eff}/g_p$. The solid-line curve of Fig. 8 shows a fit of the theory to the data in which c is determined from the specific-heat data, $d=1.27$, and $N_f(0)U_{eff}=0.27$.

An alternate empirical way to describe the effects of the Coulomb repulsion term is to fit the data with the McMillan formula[23]:

$$g=1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)],$$

where λ is the attractive electron-phonon term and μ^* is the screened Coulomb repulsion. If we choose the Coulomb term for pure Th, μ_p^*, to be

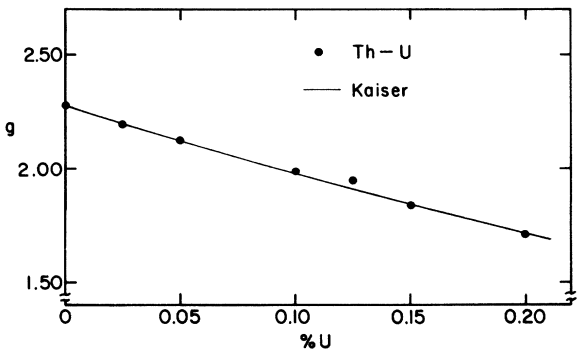

FIG. 8. Concentration dependence of the effective coupling constant g where $T_c=\Theta_D e^{-1/g}/1.45$.

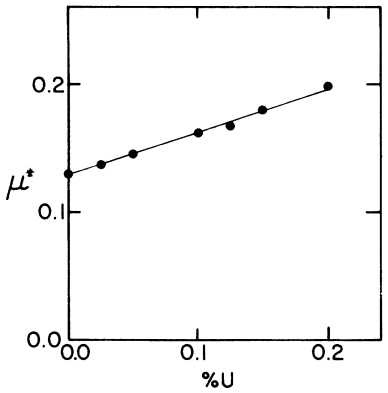

FIG. 9. Concentration dependence of McMillan's Coulomb repulsion term μ^* assuming the electron-phonon term λ is a constant.

0.13 as suggested by McMillan, then the electron-phonon term for pure Th, λ_p, is 0.54. *A priori*, there is no way to know whether T_c decreases because λ decreases or because μ^* increases but there is a clue that λ is fairly constant in that γ changes very little. λ is rather large for Th so a radical change in λ would change the mass enhancement and thus change γ. In addition, the whole Anderson picture of resonant states depends on rather large Coulomb repulsion. Hence for this analysis we attribute the changes to μ^*. If one then assumes that the electron-phonon term is unaffected by the addition of uranium, that is, $\lambda=\lambda_p$, then one can calculate values for an effective μ^* for each alloy. As shown on Fig. 9, μ^* is linear in concentration and approximately doubles its value as 0.2-at.% uranium is added.

SUMMARY

The very rapid depression of the superconducting transition temperature of thorium with the addition of uranium is caused by an interaction which is time-reversal invariant as evidenced by the fact that the critical-field curves follow BCS over a wide range of concentrations. For these alloys the change in the density of states is rather small so the major effect probably is caused by changes in the relative strengths of the attractive electron-phonon interaction and the repulsive Coulomb interaction. Spin scattering, if it is present at all, is a much smaller effect than the Coulomb repulsion.

Nonmagnetic resonant impurity states can be extremely detrimental to superconductivity even though they have no local moment and show no sign of lifetime broadening of the Cooper pairs. The same Coulomb repulsion which tends to produce a local moment on the impurity site[1] can weaken the attractive interaction responsible for superconductivity[12] even though the strength of the Coulomb re-

pulsion is too small to form a local moment. Many details of the process by which the uranium impurities diminish the strength of the superconducting interaction are still unknown, of course, but the basic ideas of Berk and Schrieffer[24] and Morandi[25] probably apply. Other theoretical models, the temperature-dependent spin-scattering-rate model of Bennemann,[8] the crystal-field model of Keller and Fulde,[9] and the Kondo models of Müller-Hartmann and Zittartz[10] and Maki[11] do not seem to be appropriate for *Th*U.

ACKNOWLEDGMENTS

The authors would like to thank J. S. Fritz's group for detailed chemical analyses of the samples. J. R. Clem and M. B. Maple have made important contributions to this work.

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