Anisotropy of the Superconducting Energy Gap in Th†

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A value of the mean-square anisotropy constant $\langle a^2 \rangle$ for the superconducting energy gap of thorium has been determined from the depression of the critical temperature as carbon impurity is added. The results indicate that $\langle a^2 \rangle = 0.021$ and that the valence effect for carbon in thorium is negligible. The effect of anisotropy on the critical-field curves of Th-Gd alloys is discussed in detail.

INTRODUCTION

A DETAILED analysis of the effect of small amounts of impurity on the properties of a superconducting material must include a study of the anisotropy of the energy gap. If the impurities are nonmagnetic,[1] anisotropy effects can be the dominant consideration, especially in the low concentration region where the normal-state electronic mean free path l is larger than the superconducting coherence distance ξ. Tin, for example, shows variations in the superconducting energy gap at different parts of the Fermi surface which are typically 10% of the value of the gap; if small amounts of indium impurity are then added, there is an abrupt drop in the superconducting critical temperature T_c which is almost entirely caused by a smoothing of the energy gap due to impurity scattering.[2,3]

If the impurities are magnetic, however, the situation is quite different. Here lifetime broadening of states is the dominant factor and the anisotropy effects, although still present, play a relatively smaller role. In a recent publication, Decker and Finnemore (DF)[4] presented a careful study of the changes in the critical-field curve H_c of Th as a small amount of the magnetic impurity Gd was added. They found that pure Th exhibits a critical-field curve very close to that predicted by the Bardeen-Cooper-Schrieffer (BCS) theory and that the alloys show gapless superconductivity, a full Meissner effect, and in general follow the theories of Abrikosov-Gor'kov (AG)[5] and Skalski, Betbeder-Matibet, and Weiss[6] to an accuracy of better than 1%. Even though magnetic scattering and lifetime broadening dominates the changes in the superconducting properties, there must be some additional effects from the nonmagnetic scattering processes through changes in the anisotropy of the energy gap. For this particular alloy system, the mean free path for magnetic scattering is over 100 times longer than the mean free path for nonmagnetic scattering,[4] so that there might be measurable changes in anisotropy even for impurity concentrations as small at 0.2%.

This paper presents a measurement of the changes in the anisotropy of the energy gap of thorium with the addition of the nonmagnetic tetravalent impurity carbon. The shifts in T_c are analyzed in terms of the theory of MK and the resulting changes in critical-field curves are deduced from the theoretical work of Clem.[7] These results are then compared with the rather drastic shifts which were observed by DF for the magnetic scattering case.

EXPERIMENTAL

Sample Preparation

Samples were prepared by arc-melting thorium with high-purity spectroscopic graphite to form four different specimens with 112, 200, 400, and 1000 ppm carbon. The arc-melt buttons were then cut and swaged into cylindrical shapes 1 in. long and 0.100±0.001 in. in diam. They were then annealed at 800°C for 1 h and electropolished. The final specimens were analyzed and found to contain less than 0.02% oxygen and 0.003% nitrogen. One additional specimen included with these results is the Th^{35} sample described earlier in the work by DF.

Apparatus

The superconducting phase transitions were detected by a mutual inductance technique in which a 33-Hz ratio transformer bridge was used to detect changes in susceptibility. Temperatures were determined from the vapor pressure[8] of He^4 and magnetic fields uniform to 1 part in 10 000 over the volume of the sample were provided by a solenoid described earlier.[9] Normal-state electrical resistivity measurements were made at 4.2 and 300 K by a four-probe technique with measuring currents of about 1 A.

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RESULTS AND DISCUSSION

Depression of T_c

Susceptibility data for four of the Th-C alloys and one nominally pure Th sample are shown in Fig. 1. There is a sharp depression of T_c as the impurity concentration increases and there is also a significant broadening of the transition which presumably arises from inhomogeneity in the carbon concentration. This inhomogeneity in turn complicates the definition of T_c for a given sample and it is necessary to define an average T_c which hopefully corresponds to the measured electrical resistivity, another average quantity. For this work T_c is arbitrarily defined to be the average of two temperatures; the temperature at which the normalized susceptibility is 0.5 and the temperature given by the midpoint of a line through the steep portion of the curve. These two temperatures are very nearly equal and, in addition, T_c defined in this way agrees with an extrapolation of the critical-field curves to zero magnetic field within an accuracy of 0.002 K.

A plot of the shift in critical temperature ($\delta T_c = T_c - T_{cp}$, where T_{cp} is the transition temperature of the ultrapure Th sample reported by DF[4]) versus the electrical resistivity ratio

$$\rho = \frac{\rho_{4.2\text{ K}}}{\rho_{273\text{ K}} - P_{4.2\text{ K}}},$$

in Fig. 2 shows an initial sharp drop in T_c and a subsequent leveling off to a smaller slope similar to the results obtained by Serin and co-workers[1] for other alloys. The error bars represent the temperature range from a normalized susceptibility of 0.2 to 0.8. If the data are cast in the form of a $\delta T_c/\rho$-versus-$\ln\rho$ plot (Fig. 3) as suggested by the work of MK and Ginsberg,[10] there is a fairly good fit to the theory with no valence effect correction. A fit of the data to the approximate expression for the theory,

$$\delta T_c = A\rho + B\rho \ln\rho, \tag{1}$$

where A and B are constants related to the mean square anisotropy constant $\langle a^2 \rangle$ and factors related to the valence effect,[3,10] gives $A = -0.014$ and $B = 0.255$.

In order to determine a numerical value for $\langle a^2 \rangle$, the data were fit directly to the full MK expression

$$\delta T_c = T_c \langle a^2 \rangle I_c(\chi), \tag{2}$$

where

$$I_c(\chi) = -\int_0^{2\omega_D/kT_c\chi} \frac{\tanh(\frac{1}{4}\chi y)}{y(1+y^2)} dy, \tag{3}$$

$$\chi = \alpha^i \rho, \tag{4}$$

ω_D is the Debye frequency, k is the Boltzmann constant, and α^i is a constant for a given host and impurity. The quantity χ, as defined by MK, is directly related to the

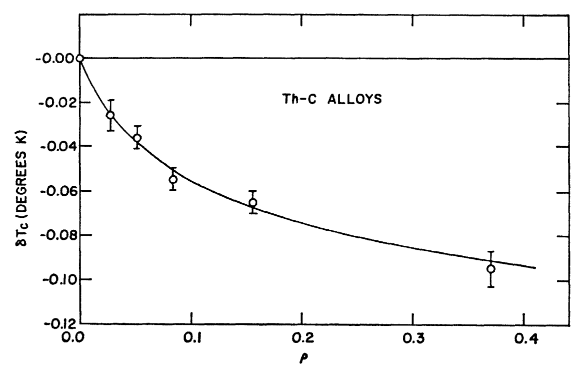

FIG. 2. Depression of T_c as a function of the ρ. The solid line is the best fit of these data to the theory of MK. For this line $\langle a^2 \rangle = 0.021$ and $\alpha^i = 110$.

mean time required for collisions to smooth the anisotropy of the energy gap and hence is proportional to the electrical resistivity. A fit of the data which minimizes the square deviation from Eq. (2) gives $\langle a^2 \rangle = 0.021$ and $\alpha^i = 110$. This curve is shown by the solid line of Fig. 2.

As would be expected, these values are in good agreements with the approximate expression of Eq. (1). If the valence-effect constant[10] $K^i\alpha^i$ is evaluated from the measured value[10] of A through the relation

$$A = K^i\alpha^i + \langle a^2 \rangle T_c \alpha^i (-0.36 + 0.078 \ln\alpha^i), \tag{5}$$

then $K^i\alpha^i$ is found to be 0.02. This is about two orders of magnitude smaller than the valence effect for In alloys[10] where $K^i\alpha^i$ is approximately equal to 2.0. It would appear then that carbon impurities in Th neither give up electrons to the conduction band nor take them out. Our present picture for the carbon impurity is that carbon atoms are bound at interstitial sites in such a way that they do not appreciably change the conduction bands.

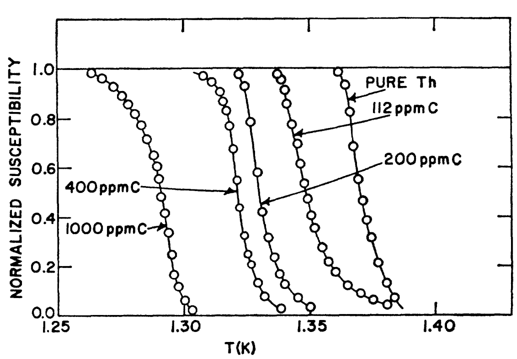

FIG. 1. The superconducting transitions in zero magnetic field for a series of Th-C alloys.

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Changes in H_c versus T

In addition to the changes in T_c, the anisotropy effects also can make small but measurable changes in the critical-field curve. In view of the fact that the changes are rather small, it is convenient to represent the changes in terms of deviations from a fiducial parabola by means of the expression

$$D(t)=H_c/H_0-(1-t^2), \qquad (6)$$

where H_0 is the value of H_c at $T=0$ and $t=T/T_c$. As shown in Fig. 4, the critical-field curve for a superconductor with $\langle a^2\rangle=0.021$ (dot-dash line) lies below

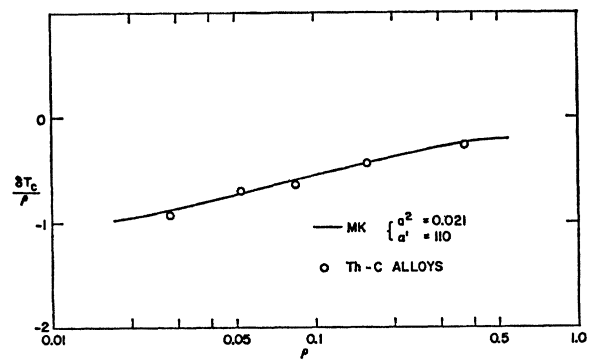

FIG. 3. A plot to determine the magnitude of the valence effect.

the BCS curve (solid line) by about 0.7%. Measurements by DF for the critical-field curve of pure Th lies well above the $\langle a^2\rangle=0.021$ curve and presumably the difference between these two arises from strong-coupling effects.[11]

Decker and Finnemore also made a detailed study of the shift in critical-field curves for superconductors doped with the magnetic impurity Gd, and found large deviations which could be attributed to lifetime

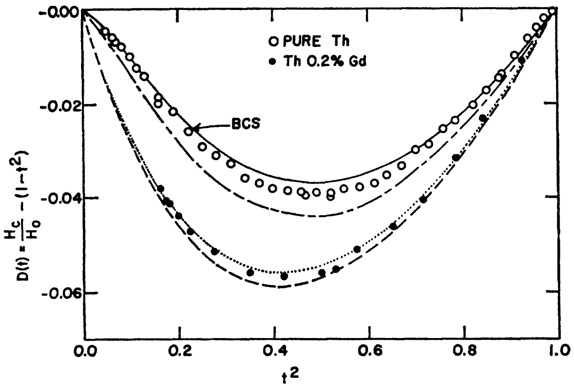

FIG. 4. Deviation functions for pure Th and Th-0.20 at.% Gd. The dot-dash curve is Clem's prediction for a pure superconductor with $\langle a^2\rangle=0.021$. The dashed curve is the AG prediction for Th-0.20 at.% Gd. The dotted curve is the AG prediction after it was corrected for anisotropy effects.

broadening effects. In the original analysis of these data, the ratio of T_c of the alloy to T_c of pure Th was used to determine the lifetime broadening parameter[6] and the AG theory[5,6] was used to calculate the critical-field curve. Results of this calculation for the Th-0.2 at.% Gd sample shown by the dashed line of Fig. 4 are in rather good agreement with the measurements. If account is also taken of the smoothing of the anisotropy of the energy gap using the measured value of $\rho=0.0544$ and $X=6.05$, then one obtains the dotted curve of Fig. 4. For this sample the mean free path is approximately equal to the coherence distance, so the shifts in critical-field curve are only about half as large as the shifts to be expected for a complete smoothing of the anisotropy of the gap. It is easily seen that the magnitude of the anisotropy effect is only about $\frac{1}{10}$ as large as the lifetime broadening effect and these corrections do not alter the original conclusions[4] about these alloys.

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