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Effect of iron impurities on the superconductivity in granular technetium

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The effect of Fe impurities on the superconductivity of Tc has been investigated with almost dirty-limit samples prepared by electrodeposition and reduction. Upper-critical-field curves show, as expected from the Mössbauer study, the existence of an exchange field due to the impurity. The observed transition-temperature depression by Fe impurities indicates that there is localized spin fluctuation in the Tc-Fe alloy. This conclusion is not consistent with the previous results found for arc-melted Tc-Fe alloys.

Because of the absence of stable isotopes, few investigations have so far been reported on the effect of magnetic impurities in superconducting Tc.[1,2] From measurements of the superconducting transition temperature T_0 Shelton *et al.*[2] have concluded that the enhanced depression of T_0 in the Tc-Fe alloy is due to the formation of a nonmagnetic resonance state, and that there is no localized spin fluctuation (LSF) present. Recently, a Mössbauer study has revealed that the dilute Fe impurity in Tc has a small induced magnetic field, -7.5 ± 1 kOe in the external field of 45 kOe at 4.2 K.[3] This suggests that the enhanced depression of T_0 may be attributed to the LSF.

For further information on the magnetic character of Fe impurities in Tc, we prepared almost dirty-limit metallic Tc. The reason for preparing dirty samples are as follows. First, since the electron mean free path is short in dirty samples, the interaction between impurities is suppressed, and consequently a single-impurity effect can be observed. Second, the upper critical field H_{c2} should be much larger than that of a pure bulk structure and hence observations of the effect of magnetic impurities on H_{c2} becomes easier. In this paper, we report measurements of H_{c2} and T_0 with almost dirty-limit Tc samples containing very dilute 3d impurities (Fe,Co, Mn). Comparisons with relevant works and a discussion are also given.

Preparations of extremely dirty samples are usually made by sputtering or evaporation. However, because of the difficulties associated with its handling, we have developed a method to prepare almost dirty-limit metallic Tc by means of electrodeposition and reduction, of which details were previously reported.[4] Technetium and 3d impurities were electrolytically deposited on a thin film of iron-free nichrome (1.7×8.0 mm^2, vapor deposited on a ceramic base). For electrodeposition, we used Tc in the chemical form of $NH_4{}^{99}TcO_4$ in aqueous solution. As impurities, we used Fe in the chemical form of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, Co in $CoCl_2 \cdot 6H_2O$, and Mn in $MnCl_2 \cdot 4H_2O$. Technetium and one of these impurities were simultaneously electrodeposited in H_2SO_4 electrolyte (pH 1.0), which contained tracer amounts of radioactive isotopes, ^{55}Fe, ^{57}Co, and ^{54}Mn, respectively. By adding the electrolyte during deposition, the change in ion concentration was minimized. To eliminate technetium-oxide and some dissolved gases, the samples were then heat treated in a highly purified hydrogen atmosphere for 4 h at 1000 ° C. The amounts of ^{99}Tc and impurities recovered from the electrolyte were determined by measuring the activity of the residual solution with a liquid scintillation counter (^{99}Tc), a Si (Li) detector (^{55}Fe), a pure Ge detector (^{57}Co) and a Ge (Li) detector (^{54}Mn). The thickness of samples thus prepared was 8–9 μm. The impurity concentration was 0.25 at. % at maximum.

As we used a granular nichrome (1.5–3.5 μm diam) film as the substrate, Tc electrodeposited on it also had the granular structure. Analysis by a scanning electron microscope showed that the metallic Tc produced was granular having a diameter of 2.1–2.9 μm. From the width of x-ray diffraction lines, the grain size was estimated to be about 500 Å and more. An x-ray diffraction study confirmed the hcp structure of metallic Tc ($a = 2.74$ Å, $c = 4.40$ Å). Impurity analysis was made by using an x-ray microprobe analyzer. Diffusion of the basic nichrome into Tc was not over the threshold for detection, 100 ppm for Ni, and no appreciable maldistributions of Fe, Co, and Mn in the host were observed.

As the first step, T_0 was measured by both the ac resistive (four-probe) and the inductive method. For pure Tc, T_0 was found as 7.46 ± 0.02 K by both methods, but for others containing impurities, T_0 obtained by the inductive method was slightly smaller (<2%) than that by the ac resistive method. This difference may be due to some inhomogeneity in these samples, but was considered not to be critical for the present experiment. Henceforth, measurements of H_{c2} and T_0 were

performed by the ac resistive method, where measuring current was 10 μA, 1 kHz.

Figure 1 shows temperature dependence of H_{c2} for three kinds of samples, pure Tc, Tc-Fe(0.14 at.%), and Tc-Fe(0.21 at.%). The applied field was perpendicular to the sample surface. At fixed temperatures ($<\pm 5$ mK), the field was increased until the superconductivity was quenched. The value of H_{c2} was defined as the field at which the resistivity reached half its normal-state value. The amount of hysteresis was never greater than 4% of H_{c2}. The width of the transition was approximately 10% of H_{c2}. The residual resistivity is about 100 $\mu\Omega$ cm and the value of Γ is 2.2–2.5, where Γ is the ratio of resistance at 295 K to that at 8 K. The large value of residual resistivity and the small value of Γ compared to usual bulk samples prove that the present samples have very dirty structure. To see only the effect due to Fe impurities, H_{c2} was corrected for Γ by a similar method made by Chaikin and Mihalisin.[5]

As seen in Fig. 1, $H_{c2}(0)$ for pure Tc is 29 kOe, which is about ten times larger than that reported for arc-melted pure Tc, 2.6 kOe.[6] The curves show upward curvature near T_0. A similar curvature was also reported for a dirty granular Al film.[7] As pointed out in Ref. 7, this upward curvature seems to be a structural effect appearing in granular samples, but more data are needed to get the conclusion on its origin.

In the case of dirty-limit superconductors, the slope of $H_{c2}(T)$ for $|T - T_0| \ll T_0$ is given by[8]

$$\frac{dH_{c2}}{dT} = -\frac{12k_B c}{\pi v_F e l}, \tag{1}$$

where k_B is the Boltzmann constant, v_F is the Fermi velocity of Tc and l is the electron mean free path. Using[9] $v_F = 1.8 \times 10^8$cm/sec in Eq. (1), we get $l = 5$ Å, confirming the almost dirty-limit structure of the present samples. This value of l is much smaller than the grain size (≥ 500 Å), suggesting that the electrons are mainly scattered by lattice defects in a grain.

The effect of magnetic impurities on a dirty superconductor can be expressed by the pair breaking parameter $\alpha(T)$, which is related to H_{c2} by[5]

$$\left(\frac{\alpha(T)}{\alpha_{cr}}\right)_{imp} = \frac{[H_{c2}(T)]_{pure} - [H_{c2}(T)]_{alloy}}{[H_{c2}(0)]_{pure}}, \tag{2}$$

where α_{cr} is the critical value of pair breaking required to depress T_0 to zero. Figure 2 shows the observed values of $[\alpha(T)/\alpha_{cr}]_{imp}$ divided by concentration n as a function of temperature. As seen in Fig. 2, $(1/n)[\alpha(T)/\alpha_{cr}]_{imp}$ is approximately independent of Fe concentration and increases as temperature decreases. The temperature dependence cannot be explained without taking into consideration that Fe impurities in Tc are not simply nonmagnetic. As mentioned before, the Mössbauer measurement[3] has proved that the Fe impurity in Tc has a small negative induced magnetic field. This induced field at Fe nuclei corresponds to the induced magnetic moment at Fe atoms. Therefore, for the applied field near H_{c2}, the effective field is the sum of the applied field and the exchange field due to the induced moment, resulting in depression of the observed values of H_{c2} in the low-temperature region.

Figure 3 shows $\ln(T_0/T_{c0})$ versus the impurity concentration n of Fe, Co, and Mn, where T_{c0} is the transition temperature of pure Tc. The values of T_0 were taken as the midpoint of the resistive transition, of which the width was

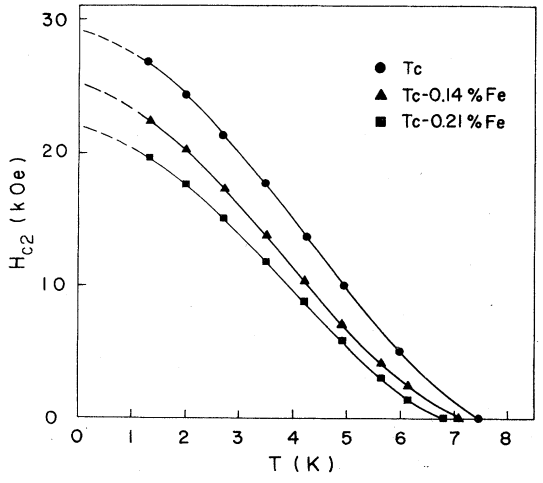

FIG. 1. Upper critical field H_{c2} vs temperature T observed for pure technetium and two Tc-Fe alloys.

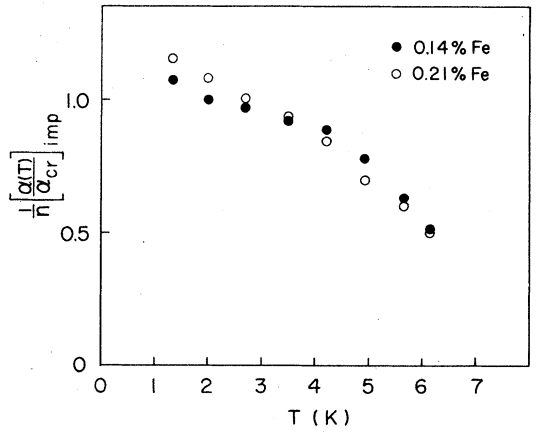

FIG. 2. Variation of $[\alpha(T)/\alpha_{cr}]_{imp}$ divided by the impurity concentration n as a function of temperature.

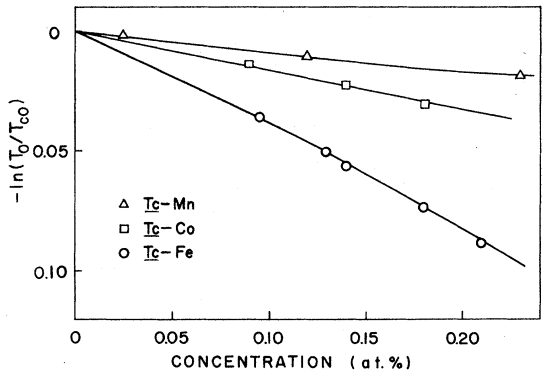

FIG. 3. Variation of $\ln(T_0/T_{c0})$ as a function of impurity concentration n for Fe, Co, and Mn.

about 0.1 K.

The initial decreases in T_0 with respect to n, $-(dT_0/dn)_{n\to 0}$, are 2.9, 1.2, and 0.6/K at. % for Fe, Co, and Mn, respectively. The Fe impurity in Tc depresses T_0 more rapidly than the other solutes, as has been found for Ru-3d,[10,11] and Ir-3d,[12] systems. However, our values are about three times larger than those by Koch *et al.*[1] with arc-melted Tc, i.e., 0.85 and 0.47 K/at. % for Fe and Co, respectively. More recently, Shelton *et al.*[2] of the same group also reported smaller values than ours.

In addition, by comparing their results for Fe impurities with Kaiser's theory,[13] they have concluded that there is no LSF in the Tc-Fe alloy. For the superconducting LSF system, it has been revealed both experimentally[12] and theoretically[14] that the initial decrease in $\ln(T_0/T_{c0})$ with respect to n is nearly linear. The present result for Fe impurities is slightly downward or linear within experimental errors (not upward as reported in Ref. 2), suggesting that the Tc-Fe alloy is the LSF system.

The possible explanations of the discrepancy between our results and the previous ones for Fe impurities are these: First, the Kaiser's theory assumes that there is no significant interaction between different impurity sites. But, they used impurity concentrations of several at. % up to 8 at. % for which the effect of the interaction between impurities should be there. Second, the above discrepancy in $(dT_0/dn)_{n\to 0}$ suggests that the pair breaking by Fe impurities is enhanced in almost dirty-limit Tc. The reason for this enhancement can be understood if the effect of LSF associated with Fe impurites increases in dirty Tc. In other words, for the extremely short mean free path of electrons, the interaction between impurities which tends to suppress the effect of LSF rarely takes place.[15] The enhancement of pair breaking by magnetic impurities in disordered superconducting systems has also been reported.[16]

It is worthwhile to note that the Ir-Fe alloy which is the well established LSF system, shows a quite similar magnetic character to our case. The Fe impurity in Ir has a small induced magnetic field, −8.6 at 45 kOe and 4.2 K,[17] and the value $-(dT_0/dn)_{n\to 0}$ is 2.06 K/at. %.[12] Since the structures in Ref. 17 are not the same, direct comparison of the above two cases cannot be made, but the similarity is still indicating further studies.

Experimental evidence and the above discussion seem to support the conclusion that there is localized spin fluctuation in the Tc-Fe alloy and that the enhanced depression of T_0 by Fe impurities is attributed to LSF. For further information, a Mössbauer study on Tc-Fe alloys is in progress.

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