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Superconducting and Magnetic Properties of Dilute Tc-(Fe) Alloys

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The superconducting transition temperature T_0, the upper critical field H_{c2}, and the hyperfine field have been measured for dilute Tc-Fe alloys. The samples prepared by electrodeposition and reduction have an almost dirty limit structure. The linear decrease in $\ln T_0$ with respect to the impurity concentration is consistent with the theoretical prediction for the localized spin fluctuation system. Observed curves of $H_{c2}(T)$ and the small negative value of the saturation hyperfine field indicate that Fe impurities in Tc do not have well defined magnetic moment, and that there exist localized spin fluctuations in the Tc-Fe system. This conclusion is not consistent with the previous results found for arc-melted Tc-Fe alloys.

KEY WORDS Superconductor/ Technetium/ Critical temperature/ Upper critical field/ Localized moment/ Mössbauer effect/

INTRODUCTION

In the years after the paper of Clogston *et al.*,[1] considerable effort has been devoted, both experimentally and theoretically, to understand the magnetic properties of transition metal alloys with 3d transition metals as impurities.[2] In particular, a number of studies have been reported on the effect of 3d impurities on the superconducting property of 4d or 5d transition metals.[3~5] However, because of the absence of stable isotopes, few investigations have so far been reported on the Tc host alloys. Koch *et al.*[6,7] reported that the magnetic susceptibility of Tc-3.7 at.%Fe is almost independent of temperature and that the suppression of transition temperature and enhancement of susceptibility by Fe impurities are much more than those caused by Co and Ni impurities. From their results, the magnetic character of Fe impurities in Tc is expected to be in the transition region from the non magnetic to the magnetic state. They used impurity concentrations of several at.% up to 8 at.%, for which the effect of the interaction between impurities has to be taken into account, and direct comparisons with the Kaiser's theory[8] on the impurity concentration dependence of transition temperature are not appropriate. By this reason, it seems to be worthwhile to investigate the superconducting and magnetic properties with the extremely dilute impurity system of Tc. For better understanding of the dilute Tc-Fe alloys, we have measured the superconducting transition temperature T_0 and the upper critical field H_{c2} of Tc-3d (Fe, Co, Mn) alloys, and also the Mössbauer hyperfine field H_{hf} of ^{57}Fe impurities in Tc. Some of the results were

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previously reported.[9,10]

The impurity concentration dependence of T_o and of $H_{c2}(T)$ reflects magnetic behaviors of the impurity in the host in question. In the transition region between the magnetic and the non magnetic state, the suppression of T_o by magnetic impurities has been explained either by the localized spin fluctuation (LSF) model[11] or by the non magnetic resonance model.[8] In addition, the measurement of H_{hf} is a good mean to probe the 3d magnetization, because H_{hf} is assumed to be proportional to the electronic polarization localized on the impurity site. Since the Mössbauer measurement is feasible with very dilute samples (in a low-ppm region), it is possible to obtain information of a single impurity (non-interacting to each other) by means of this method.

In this paper, we present our experimental results of T_o, H_{c2}, and H_{hf} obtained with extremely dilute Tc-Fe alloys having an almost dirty limit structure. Comparisons with the results for well studied 4d-Fe and 5d-Fe systems, and with predictions of the LSF model are also given.

EXPERIMENTAL

1. Sample Preparation

In order to prepare metallic Tc, we have developed a method of sample preparation by means of electrodeposition and reduction, of which the details were previously reported.[12] Technetium and 3d impurities were electrolytically deposited on a thin film of iron free nichrome ($1.7\times8.0\,mm^2$, 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 $FeSO_4(NH_4)_2SO_4\cdot6H_2O$, Co in $CoCl_2\cdot6H_2O$, and Mn in $MnCl_2\cdot4H_2O$. 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 disolved 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), an intrinsic 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.

For the Mössbauer measurement, a source of ^{57}Co incorporated in Tc was prepared by a similar method. The carrier free ^{57}Co (in $CoCl_2$) and Tc (in NH_4TcO_4) were simultaneously electroplated on a Tc film previously electroplated on a Cu substrate ($150\,mm^2$). The sample was reduced for 46 h at 900°C. The radioactive intensity of ^{57}Co was 35 μCi, corresponding to 0.5 ppm of the host Tc. Although the concentration of ^{57}Co is extremely small in terms of the optimum Mössbauer condition, the effect of interactions between Fe impurities can be conveniently neglected.

An X-ray diffraction study of these samples confirmed the hcp structure of metallic Tc, and revealed that the c-axis is preferentially oriented perpendicular to the sample surface. Analysis by a scanning electron microscope showed that the metallic Tc pro-

duced on the nichrome base was granular having a diameter of 2.1～2.9 μm. 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.

2. Measurements of T_o and H_{c2}

The transition temperature T_o was determined by measuring the ac resistance as a function of temperature. The value of T_o was taken as the midpoint of the transition. A detailed description of the measuring techniques is given in ref. 12. The conventional ac four-probe technique was employed, where the current through the sample was 10 μA, 1 kHz. The temperature of samples was measured with a calibrated Ge thermometer.

Measurements of T_o were also performed by the inductive method. For pure Tc, T_o was determined as 7.46±0.02 K by both methods (ac resistive and inductive), but for others containing impurities, T_o obtained by the inductive method was slightly smaller ($<2\%$) than that by the ac resistive method. This difference may be due to some

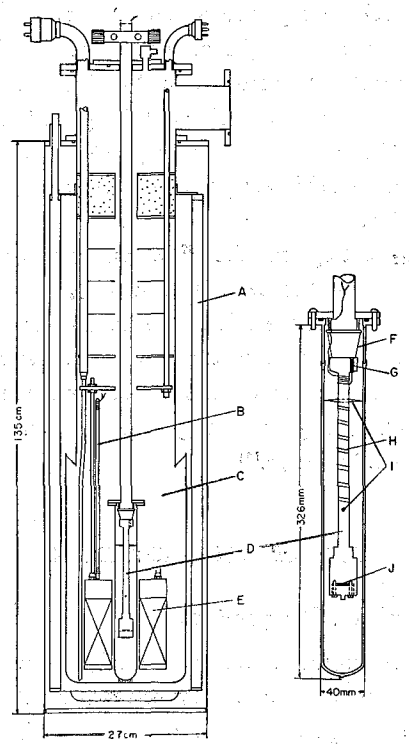

Fig. 1. Schematic diagram of the cryostat for measurements of the upper critical field. A) Liquid nitrogen, B) Level meter of liquid helium made by Nb-Ti superconducting wire, C) Liquid helium, D) Copper sample holder, E) Superconducting magnet, F) Silk thread, G) Ge thermometer, H) Heater (manganin wire), I) Bamboo needle, J) Sample. Radiation shields around the sample room are not shown in the figure.

inhomogeneity in these samples, but was considered not to be critical for the present experiment.

The upper critical field $H_{c2}(T)$ was determined by measuring the resistive transition of samples. The experimental arrangement is shown in Fig. 1. The external magnetic field supplied by a superconducting magnet was perpendicular to the sample surface. The sample holder made by copper was arranged so as to eliminate the temperature difference between the sample and the Ge thermometer, and to minimize the effect of the magnetic field to the thermometer. At a fixed temperature ($<\pm 5$ 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}.

3. Mössbauer Measurements

The Mössbauer experiment was performed in the temperature range of 1.5~4.2 K and in the external magnetic field H_{ext} up to 50 kOe. From measurements of H_{c2}, it was confirmed that the superconducting state was definitely quenched in the magnetic field applied here. The sample was placed at the center of a superconducting magnet and was attached to a copper holder by Apiezon N grease. Temperature measured by vapor-pressure of ^{4}He was stable to better than 2% during measurements of about 10 h. The absorber used was stainless steel containing 1.0 mg/cm^2 of ^{57}Fe, which was kept at room temperature. The calibration of the velocity was made by the known magnetic splitting of α-Fe. The external field was perpendicular to the sample surface and was parallel to the γ-ray direction.

The effective field H_{eff} acting on the ^{57}Fe nucleus contained in the sample as impurities is given by the sum of the external field H_{ext} and the induced hyperfine field H_{hf}, *i.e.*, $H_{eff}=H_{ext}+H_{hf}$, of which the value is determined from the hyperfine spectra. By taking into account the existence of texture in the present sample, analysis of the spectra was made by assuming the Lorentzian line shape and the ideal intensity ratio of 3:0:1:1:0:3. This assumption is good enough for estimations of H_{eff}, because of the small quadrupole splitting, -0.13 mm/s.[10]

RESULTS AND DISCUSSION

1. Superconducting Transition Temperature

In Fig. 2 are shown the superconducting transition curves of pure Tc and three samples containing Fe impurities, observed by the ac resistive method. The observed curves involve the resistive change in the nichrome base. However, because of the small change in resistivity of the nichrome film, being less than 3% from 293 K to 4.2 K, this effect can be neglected. As seen in the figure, for pure Tc, a sharp transition is observed at $T_o=7.46$ K, where the transition width is about 0.1 K. For the Tc-Fe system, broader transition curves were observed, proving the existence of some inhomogeneity in these samples. The residual resistivity is 100~200 $\mu\Omega$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

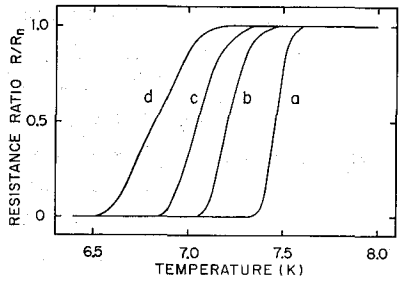

Fig. 2. Typical transition curves (resistance versus temperature) for various Tc-Fe alloys. a) Pure Tc, b) Tc-0.10 at.% Fe, c) Tc-0.14 at.% Fe, d) Tc-0.21 at.% Fe.

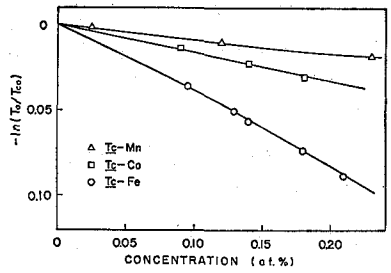

Fig. 3. Logarithmic value of the reduced transition temperature, $\ln(T_o/T_{co})$, versus the impurity concentration n for Tc-Fe, Tc-Co, and Tc-Mn alloys.

resistivity and the small value of Γ compared to usual bulk samples prove that the present samples have very dirty structure.

In Fig. 3 is shown $\ln(T_o/T_{co})$ versus the impurity concentration n of Fe, Co, and Mn, where T_{co} is the transition temperature of pure Tc. The initial decrease in T_o with respect to n, $-(dT_o/dn)_{n\to 0}$, are 2.9, 1.2, and 0.6 K/at.% for Fe, Co, and Mn, respectively. Our values for Tc-Fe and Tc-Co are about three times larger than those by Koch *et al.*[6] with arc-melted samples, *i.e.*, 0.85 and 0.47 K/at.%. Discussion about this discrepancy will be given below. In both experiments, however, the Fe impurity suppresses T_o more intensely than others. This suggests that the magnetic nature of Fe impurities has the responsibility for suppression of T_o. In the systems of Ru-3d and of Ir-3d, a similar behavior has been reported. The initial decreases of T_o are 0.28 and 2.06 K/at.% for Ru-Fe[4] and Ir-Fe,[5] respectively. These systems are known to be the LSF system from both the impurity concentration dependence of T_o[5,13] and the temperature dependence of resistivity.[14,15]

According to the LSF model, a localized spin at the impurity site fluctuates with a characteristic frequency $w_{sf}=k_B T_{sf}/\hbar$, where T_{sf} is spin fluctuation temperature regarded as a phenomenological parameter, and the electron scattering by LSF at the impurity site is responsible for the suppression of T_o. Recently, Rössler and Kiwi[11] proposed a formula for T_o as a function of n,

$$T_o=T_{co}\exp[-An(1-Bn)], \tag{1}$$

where

$$A=\frac{(2l+1)\alpha_o z}{\pi\Gamma N(0)}\left[1+\frac{(K_o+5/6)(\Gamma/z\Gamma_s)}{1+\Gamma^2 a_\infty}\right], \tag{2}$$

$$B=\frac{(2l+1)}{\pi\Gamma_s N(0)}\cdot\frac{\alpha_o+5/6+\Gamma^2 a_\infty}{1+\Gamma^2 a_\infty}. \tag{3}$$

Notations used in the above relations are given in ref. 11. Equation (1) is a generalization of the Kaiser's theory, *i.e.*, the LSF effect is taken into account in this case. From the equation, the initial decrease in $\ln(T_o/T_{co})$ with respect to n is nearly linear. The present result for the Tc-Fe system is, as seen in Fig. 3, slightly downward or linear, suggesting that Tc-Fe alloys be the LSF system.

The discrepancy in $(dT_o/dn)_{n\to 0}$ between the present experiment and the previous ones[6,7] indicates 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 impurities increases in dirty Tc. In other words, for extremely short mean free path of electrons, the interaction between impurities which tends to suppress the effect of LSF rarely takes place.[16]

2. Upper Critical Fields

The temperature dependence of H_{c2} for three kinds of samples, pure Tc, Tc-Fe (0.14 at.%), and Tc-Fe(0.21 at.%) has been measured. As shown in Fig. 4, $H_{c2}(0)$ for pure Tc is 29 kOe, which is about 10 times larger than that reported for arc-melted pure Tc, 2.6 kOe.[17] The large value of $H_{c2}(0)$ observed here is due to the very dirty structure of our sample. In the case of dirty limit superconductors, the slope of $H_{c2}(T)$ for $|T-T_o| \ll T_o$ is given by[18]

$$\frac{dH_{c2}}{dT} = -\frac{12k_B c}{\pi v_F e l}, \tag{4}$$

where k_B is the Blotzmann constant, v_F is the Fermi velocity of Tc and l is the electron mean free path. Using $v_F = 1.8\times 10^8 \mathrm{cm/s}$[19] in Eq. (4), we get $l = 5$ Å, confirming the almost dirty limit structure. This value of l is the order of the lattice constant and much smaller than the grain size ($\geq$500 Å), suggesting that electrons are mainly scattered by lattice defects in a grain.

The temperature dependence of pair breaking (or weakening) due to impurities can be expressed by the pair breaking parameter $\alpha(T)$, which is related to H_{c2} by[20]

$$\left[\frac{\alpha(T)}{\alpha_{cr}}\right]_{imp} = \frac{[H_{c2}(T)]_{pure} - [H_{c2}(T)]_{alloy}}{[H_{c2}(0)]_{pure}} \tag{5}$$

where α_{cr} is the critical value of pair breaking required to depress T_o to zero. Our measurements indicate that $[\alpha(T)/\alpha_{cr}]_{imp}$ increases as temperature decrease. The temperature dependence can not be explained without taking into consideration that Fe impurities in Tc are not simply non magnetic. A possible explanation is that, under an applied field near H_{c2}, some effective moment is induced at the Fe impurity site and the exchange field due to the effective moments depresses the observed H_{c2} in the low

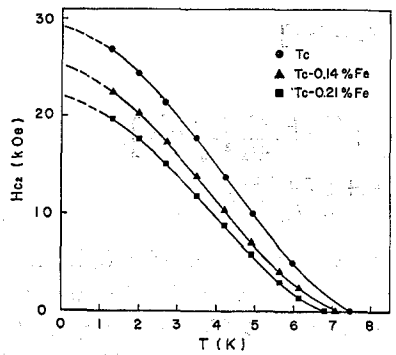

Fig. 4. Temperature dependence of the upper critical field H_{c2} for pure Tc and two Tc-Fe alloys.

temperature region.

3. Hyperfine Fields

Typical Mössbauer spectra taken at 4.2 K for different external fields are shown in Fig. 5. The solid lines are the results of a computer fit, from which the value of $H_{\rm eff}$ was obtained. A small asymmetry in the spectra is due to the quadrupole interaction. Since the concentration of ^{57}Co in the sample is very small, the statistical accuracy of the spectra is not satisfactory.

In Fig. 6 is shown $H_{\rm hf}(=H_{\rm eff}-H_{\rm ext})$ versus $H_{\rm ext}/T$ for $H_{\rm ext}=30$ and 50 kOe. From the figure, the saturation hyperfine field $H_{\rm sat}$ which depends on $H_{\rm ext}$, is estimated as -4.4 ± 1 kOe for 30 kOe and -7.4 ± 1 kOe for 50 kOe. The local susceptibility $H_{\rm hf}/H_{\rm ext}$ for $H_{\rm ext}=30$ and 50 kOe is determined as -0.145 ± 0.009 from the average of all data in Fig. 6.

The saturation hyperfine fields given above are much smaller than those for the case where an Fe impurity has a well defined magnetic moment, even for the case where the Kondo effect exists. This suggests that the Fe impurity in Tc has no well defined magnetic moment. Although $H_{\rm hf}$ includes the Van Vleck type contribution $H_{\rm v}$, being proportional to $H_{\rm ext}$, from excited electronic states, the term $H_{\rm v}$ is usually positive and is only a few percent of $H_{\rm ext}$(for example, 3% for Mo-Fe[21] and 1% for Nb-Fe,[22] both 4d hosts). In the present case, $H_{\rm v}$ was not measured, but can be ignored within experimental errors. Thus, the observed small negative $H_{\rm hf}$ is attributed to the local magnetization of Fe impurities.

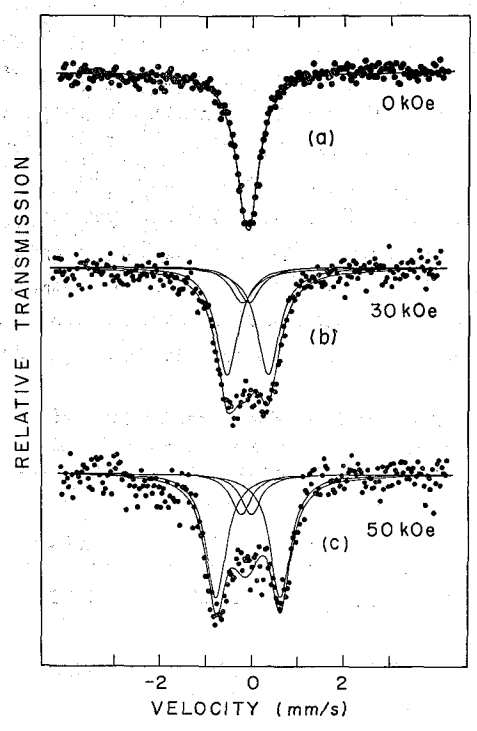

Fig. 5. Mössbauer spectra of ^{57}Fe impurities in Tc at 4.2K in different external magnetic fields. The direction of γ rays is parallel to the external field. The absorber is stainless steel containing 1.0 mg/cm^2 of ^{57}Fe.

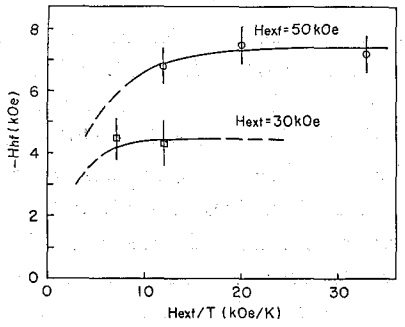

Fig. 6. Hyperfine field of ^{57}Fe in Tc from Mössbauer experiments as a function of $H_{\rm ext}/T$, where the external field $H_{\rm ext}=30$ and 50 kOe, and temperature is $1.5<T<4.2$K.

4. Comparisons with Nb, Mo, Ru, and Ir Hosts

Clogston *el al.*[1] showed from susceptibility measurements that the magnetic character of Fe impurities in the series of 4d transition metals is well correlated with the average number of outer electrons, N. However, in the measurement, they used 5d Re instead of 4d Tc. This replacement may be due to the difficulty in handling radioactive Tc. In order to understand the magnetic character of Fe impurities in Tc, it is worthwhile to compare our results with those of other well studied 4d-Fe or 5d-Fe systems.

In Table I are listed the data of initial depression of T_0 and of the saturation hyperfine field H_{sat} of Nb-Fe, Mo-Fe, Tc-Fe, Ru-Fe, and Ir-Fe systems. The value of H_{sat} determined by Mössbauer measurements is generally assumed to be proportional to the magnitude of the effective localized moment. Since H_{sat} generally depends on H_{ext}, the values found for $H_{ext}=50\sim62$ kOe are adopted in the Table.

The magnetic character of Fe impurities in Nb($N=5$, bcc) is simple non magnetic.[22,23] The initial depression of T_0 and H_{sat} are both the smallest among five systems listed in the Table. In contrast, Fe impurities in Mo ($N=6$, bcc) have a well defined magnetic moment, and indeed the Kondo effect has been observed.[21,25] Both the initial depression of T_0 and the H_{sat} are the largest among those given in the Table. In the Ru-Fe case, both values are comparable to those of Nb host, but the existence of LSF is supported by the impurity concentration dependence of T_0 and by the temperature dependence of the resistivity, from which the spin fluctuation temperature T_{sf} is estimated to be more than 700 K.[13] Judging from our results of the Tc-Fe system, the magnetic character of Fe impurities in Tc is considered to be in the intermediate region between Mo-Fe and Ru-Fe.

It is interesting to compare the results of the Tc-Fe system with those of the Ir-Fe system. In the 5d series, the critical region from the non magnetic to the magnetic state occurs at Ir($N=9$, fcc), which has been confirmed by bulk susceptibility measurements.[28] In addition, in the Ir-Fe case, the suppression of T_0[5] and the characteristic temperature dependence of resistivity[14,15] have been explained as the effect of LSF. Two different values of T_{sf} for this system have been reported, 28 K[14] and 225 K.[15]

The similarities in $-(dT_0/dn)_{n\to0}$ and H_{sat} between Tc-Fe and Ir-Fe systems indicate that the enhanced depression of T_0 and the small value of H_{sat} for the Tc-Fe system are attributed to LSF. The possible explanation for the small negative values of H_{sat} in Tc-Fe and Ir-Fe systems are as followings: In these systems, a high external magnetic field of 50 kOe or more may induce a localized spin at the impurity site. Although this

Table I. Initial Depression of Transition Temperature and Saturation Hyperfine Field of 4d-Fe and Ir-Fe Alloys. N is the Number of Outer Electrons of the Host Metal

Host	Nb	Mo	Tc	Ru	Ir
N	5	6	7	8	9(5d)
$-(dT_0/dn)_{n\to0}$ (K/at.%)	0.22[23]	$\gtrsim60$[24]	2.9	0.28[4]	2.06[5]
H_{sat} (kOe)	+1[22]	−110[25]	−7.4	−1[26]	−11.7[27]

induced spin fluctuates in time with the intrinsic frequency which is much higher than that of the nuclear Larmor precession, it spends more time in the parallel spin state to the external field. In this circumstance, Fe nuclei involved as impurities experience the time-averaged H_{hf}, which can be observed by the Mössbauer effect measurement.

CONCLUSIONS

The suppression of T_c of Tc by Fe impurities is more intense than those by other 3d impurities (Co, Mn). The linear decrease in $\ln T_c$ with respect to impurity concentration of dilute Tc-Fe alloys is consistent with the theoretical prediction for the LSF system. Observed curves of upper critical field H_{c2} of Tc-Fe alloys and the small negative value of saturation hyperfine field of ^{57}Fe in Tc suggest that an effective moment is induced at the impurity site by an external field.

Experimental evidence and discussion given in this paper lead us to the conclusion that the magnetic character of Fe impurities in Tc is the intermediate state between non magnetic and magnetic, and that there is LSF in this alloy. The present conclusion is not consistent with the previous result[7] found with arc-melted Tc-Fe alloys. However, because of the limited data so far obtained, it is difficult to draw any quantitative conclusion, such as for spin fluctuation temperature. Further studies of the Mössbauer hyperfine field and of the electrical resistivity in the extended temperature region should be considerable interest.

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