Bull. Inst. Chem. Res., Kyoto Univ., Vol. 58, No. 1, 1980

Localized Spin Fluctuations in 4d and 5d Transition Metals with Iron Impurities

Toshiro TAKABATAKE,* Hiromasa MAZAKI,* and Teruya SHINJO**

Received December 7, 1979

The superconducting transition temperatures of TcMn, TcFe, and TcCo alloys have been measured. The rapid depression of the transition temperature of Tc by Fe impurities can be understood in terms of Rössler and Kiwi's theory for localized spin fluctuations in superconducting alloys. The magnetic character of Fe impurities in Tc, Ru, and Ir hosts has also been studied by Mössbauer experiments in the temperature region of 1.4–290 K and in external fields up to 50 kOe. Saturation hyperfine fields in 50 kOe are -7.3 ± 1 kOe for TcFe, -1 ± 1 kOe for RuFe, and -9.3 ± 1 kOe for IrFe, being much smaller than those of usual Kondo alloys. A qualitative explanation of these small hyperfine fields is attempted by a stochastic model based on the LSF concept.

KEY WORDS: Localized magnetic moment / Dilute alloys / Localized spin fluctuations / Superconducting transition temperature / Mössbauer effect /

I. INTRODUCTION

The problem of the formation of localized magnetic moment in metals has received considerable attention in the last two decades. Transition metals containing Fe impurities played an important historical role. Matthias *et al.*[1,2] demonstrated from susceptibility measurements of dilute ($\sim1\%$) solutions of Fe in various 4d elements and alloys that in certain of these host metals the Fe impurities possess a localized magnetic moment, whereas in others they do not. This remarkable behavior drew Anderson's attention[3] to the local moment problem. However, at the present stage, the magnetic character of these systems is still less clear than for Fe impurities in simple metals like Cu, Ag, Au, and Al.

In the system of 4d and 5d transition metals with Fe impurities, early susceptibility measurements[2] showed that the magnetic character of Fe impurities changes from magnetic to nonmagnetic when the host changes from Mo (the number of outer electrons $N=6$) to Re (5d, $N=7$), which was used instead of 4d Tc ($N=7$), and the change from nonmagnetic to magnetic occurs when the host changes from Ru ($N=8$) to Rh ($N=9$). In 5d series, it was shown[4] that Fe impurities start to have the localized moment character when the 5d band is fuller than that of Ir ($N=9$).

As is well known, the d band of transition metals is incomplelely filled, and is

* 高畠敏郎，間嶋啓匡: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto.

** 新庄輝也: Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

narrow in comparison with the conduction band. Besides, the d states of the impurity and of the host have similar symmetries. These situations give complicated features to the scattering problem and make difficult to have a good picture of virtual d bound states in the Anderson-Friedel model.[3] The transport properties of a nearly magnetic alloy PdNi led to the concept of localized spin fluctuations (LSF) as an important scattering mechanism.[5] The concept of LSF is as followings: If the lifetime of the local magnetic moment is severely limited by the interaction with the conduction electrons, the local spin can no longer be described as spins with fixed magnitude and must be considered to fluctuate in time at a rate τ_{sf}^{-1}, where τ_{sf} is the lifetime of the spin fluctuation and a corresponding spin fluctuation temperature is defined as $T_{sf}=h/k\tau_{sf}$. When this rate is much greater than the rate that would be produced by thermal fluctuations ($T \ll T_{sf}$), the resultant magnetic moment averages over time to zero, so that the impurity appears nonmagnetic. But at higher temperatures ($T \gg T_{sf}$), where many thermal fluctuations occur in the time occupied by one spin fluctuation, the impurity behaves like a well-defined local moment.

Rivier and Zlatic[6] have applied the LSF idea to explain the strange behavior in the resistivity of RhFe and IrFe. According to their theory the resistivity due to LSF is given by a universal function of temperature T, increasing as T^2, T, and ln T. The characteristic knee occurs at T_{sf} and marks the onset of the logarithmic regime. This theory well describes the behavior of RhFe and IrFe resistivities. The value of T_{sf} was obtained as 12 K and 225 K, respectively. By a similar analysis of the resistivity of RuFe, Kao and Williams[7] have derived the T_{sf} of this alloy as more than 700 K. These studies suggest that LSF play an important role in such systems which have no well defined magnetic moments, but show feeble memories of moments in their properties.

Superconductivity is one of the bulk properties useful to extract the information on magnetic impurities because a magnetic or nonmagnetic perturbation acts very differently on a Cooper pair. In fact, measurements of the depression of the superconducting transition temperature of Ru[7,8] and Ir[9] by Fe impurities have corroborated that these alloys are LSF systems. In the case of TcFe, we have recently measured the transition temperature and the upper critical field.[10] The depression of the transition temperature by Fe impurities is much greater than that by Co and Mn impurities. The linear decrease in ln T_0 with respect to the Fe concentration is consistent with the theoretical prediction for the LSF systems.

Mössbauer measurements, employing the interaction of the electron shell of the impurity with its nucleus, provide the most localized probe to investigate the magnetization at the impurity site. This technique can be used at extremely low concentrations so that impurity-impurity interactions may in general be ignored. For example, Mössbauer studies[11,12] of Kondo systems of simple metal-Fe alloys (CuFe, AgFe, and AuFe) have provided valuable information about the magnetic behavior of these systems above and below the Kondo temperature. However, Mössbauer study of LSF systems so far published is limited to the early experiment with IrFe.[13]

Our preliminary Mössbauer experiment on TcFe[14] has revealed a small induced magnetic field, -7.5 ± 1 kOe at 4.2 K and 45 kOe, being much smaller than that of

usual Kondo systems. A more detailed and systematic Mössbauer study of the LSF systems is of interest in the light of recent experimental and theoretical developments concerning LSF. TcFe, RuFe, and IrFe alloys are of particular interest because they are all superconducting systems.

In this paper, we first describe the superconducting transition temperature of TcFe, TcCo, and TcMn alloys. These results are compared with those of Ru and Ir host alloys containing Fe, Co, and Ni impurities, and with the recent theoretical prediction. Next, the results of the Mössbauer measurements with ^{57}Fe in Tc, Ru, and Ir are presented and compared with the Mössbauer results for typical Kondo systems like CuFe and RhFe. Discussion on the magnetic character of LSF systems is given combining the data on the depression of superconducting transition temperature, and on the hyperfine field.

II. THEORETICAL APPROACHES

1. Superconducting Transition Temperature

The effect of magnetic impurities on superconductivity has received a strong attention ever since the discovery that they produce a precipitous drop in the superconducting transition temperature T_0.[15,16] Matthias *et al.*[16] studied the effect of Cr, Fe, Co, and Ni on the transition temperature of $Mo_{0.8}Re_{0.2}$ and showed that T_0 was drastically suppressed. Especially, a few tenths of atomic percent of Fe dragged T_0 from 10 K to 1 K.

Abrikosov and Gor'kov (AG)[17] developed a theory for superconductors with paramagnetic impurities assuming that exchange scattering of conduction electrons by the impurity spins may be adequately described within the first Born approximation. Their theory successfully explained the basic features of the early experiments and further predicted the striking phenomenon of gapless superconductivity.

In recent years, normal-state studies of local moments in metals have shown the assumptions on which the AG theory is founded are not applicable to many impurity–host systems. First, the supposition that the impurity spins are well defined does not apply to weakly magnetic systems in which the localized spins fluctuate with a finite frequency τ_{sf}^{-1}. Secondly, even when the impurity spins are well defined (τ_{sf} is regarded as infinite), the effect of exchange scattering of conduction electrons to higher order J^2 (the Kondo effect) becomes significant, where J denotes an effective antiferromagnetic exchange coupling parameter.

The LSF temperature T_{sf} of alloy systems belonging to the transition region from nonmagnetic to magetic state is usually much higher than T_0, and consequently impurities behave as if they are nonmagnetic in the superconducting state. The theory concerning the impurity-superconductor system which lies in the above transition regime can be divided into two classes. One is based on the idea of Friedel,[18] *i.e.*, the d-electron states to form the localized resonance states (or virtual bound states). This approach considers that in the superconducting state the impurities form nonmagnetic resonant states and lower the transition temperature slightly through the

pair weakening effect of the Coulomb repulsion between d-electrons of the impurity atom, but still do not violate the BCS law of the corresponding states. This theory gives a good description of the transition-metal impurities in simple metal superconductors, *e.g.*, Fe group impurities in Al. The other approach considers, in addition to the effect in the former theory, the existence of the LSF and its effect on the superconductivity. The latter theory is applied to describe the systems in which the effect of LSF is observed in the normal state, *e.g.*, IrFe.

Prior to discussing the effect of LSF on superconductivity, we consider the effect of nonmagnetic resonant impurity states. Kaiser[19] considered the case where the d resonance is so broad that no localized mangetic moment forms on the impurity site. According to this theory, the equation defining T_0 for these alloys is similar to the BCS equation, but the coupling constant for the pure host, $\lambda=N(0)|g|$, is replaced by a reduced effective coupling constant for the alloy, $f\lambda$:

$$T_0=1.14\Theta_D \exp(-1/f\lambda)=T_{c0}\exp[(f-1)/f\lambda], \tag{1}$$

where $T_{c0}=1.14\Theta_D \exp(-1/\lambda)$, which is the transition temperature in the BCS theory without any impurity. From Eq. (1), T_0 shows a nonlinear behavior against the impurity concentration n with the rate of suppression becoming slow for higher concentration (upward curvature), because f is reduced almost linearly with increasing n.

The Kaiser's theory has been successfully applied to the impurity concentration dependence of T_0 for nonmagnetic systems like ThCe.[20] Besides Maple[21] has demonstrated that the theory can also be applicable to systems like AlMn and ThU, where LSF are present.

Riblet[9] has measured the depression of T_0 of Ir by Fe, Co, and Ni impurities. For IrFe, in particular, the most rapid decrease of T_0 with n was observed. In order to account for the approximately exponential decrease of T_0 with n, he inserted an electron-paramagnon coupling constant λ_s in the MacMillan formula.[22] The modified expression takes the form

$$T_0=\frac{\Theta_D}{1.45}\exp\left[\frac{-1.04(1+\lambda+\lambda_s)}{\lambda-\lambda_s-\mu^*(1+0.62\lambda)}\right], \tag{2}$$

where the parameter λ is the electron-phonon coupling constant and μ^* the Coulomb pseudo potential. Assuming λ_s varies linearly with n, this expression is similar to the modified exponential relation between T_0 and n derived by Kaiser. Riblet concluded that the linear decrease of ln T_0 with n is consistent with spin fluctuations.

In recent years, Rössler and Kiwi[23,24] studied the effect of LSF on superconducting properties both in weak and strong magnetic regimes. They started with the assumption that the LSF alloy system is described by Anderson's Hamiltonian,[3] as far as its normal properties are concerned, and the BCS interaction responsible for superconductivity is added to obtain a full description of the superconducting system. The problem was formulated in two different regimes separately: (a) Weak magnetic limit (rapid spin fluctuation), such that the lifetime of the localized magnetic moment is much shorter than that of a Cooper pair ($\tau_{sf}\ll h/kT_0$), and (b) strong magnetic limit (slow spin fluctuation with $\tau_{sf}\gg h/kT_0$).

In the weak magnetic limit (a), a perturbation expansion in the Coulomb interaction parameter U can be made and the dominant electron-hole multiple scattering processes are described by means of t-matrix. The effect of LSF is described through an energy renormalization parameter z which is evaluated selfconsistently. With this approximation, one obtains the expression of T_0 as

$$\ln\left[\frac{T_0(n)}{T_{c0}}\right]=\frac{-An}{1-Bn}, \tag{3}$$

where

$$A=\frac{(2l+1)\alpha_0 z}{\pi\Gamma N(0)}\left[1+\frac{(K_0+5/6)(\Gamma/z\Gamma_s)}{1+\Gamma^2 a_\infty}\right] \tag{4}$$

$$B=\frac{(2l+1)}{\pi\Gamma_s N(0)}\cdot\frac{\alpha_0+5/6+\Gamma^2 a_\infty}{1+\Gamma^2 a_\infty}. \tag{5}$$

Notations used in the above relations are given in Ref. 23. Using these parameters, T_{sf} is given by

$$T_{sf}=\frac{\sqrt{3}\Gamma}{\pi k z}\left[1+\frac{3}{2}\left(\frac{\Gamma}{z\Gamma_s}\right)^2\right]^{-1/2}. \tag{6}$$

Equation (3) is a generalization of the Kaiser's formula to include the effect of LSF. Although the functional form of Eq. (3) is the same as that of Kaiser's, the parameters A and B have here a generalized definition. In fact, the generalized expression of A and B reduces to Kaiser's in the absence of LSF ($z=1$, $\Gamma_s\to\infty$).

In the strong magnetic limit (b), the slow spin fluctuation was treated semi-phenomenologically, generalizing the work by Zuckermann.[25] Assuming that the LSF and an exchange interaction term of $J_1\vec{S}\cdot\vec{s}$ (J_1 is the Heisenberg exchange integral) contribute additively to the conduction electron self-energy, T_0 is given by

$$\ln\left(\frac{T_0}{T_{c0}}\right)=\psi\left(\frac{1}{2}\right)-\psi\left(\frac{1}{2}+\frac{1}{\pi k T_0\tau_p}\right). \tag{7}$$

This equation has the same form as the expression of AG,[17] but here the pair lifetime τ_p is given by

$$\tau_p^{-1}=\tau_{AG}^{-1}+\tau_{LSF}^{-1}, \tag{8}$$

$$\tau_{AG}^{-1}=\frac{1}{4}n\pi N(0)J_1^2 S(S+1), \tag{9}$$

$$\tau_{LSF}^{-1}=\frac{(2l+1)n\Gamma}{2\pi N(0)\Xi^{1/2}}, \tag{10}$$

where $\Xi(T)\sim kT_0U$ is related to the zero frequency component of the t-matrix.

From our previous works,[10,14] it is predicted that in the case of TcFe, the weak magnetic limit (a) is the case. Consequently, the theoretical approach using Eq. (3) should be applied to the present case (see below).

2. Magnetic Hyperfine Field

The usefulness of the Mössbauer effect in the local moment problem was demonstrated by Kitchens *et al.*[26] They showed that the localized magnetic moment ob-

tained from the hyperfine field measurements of ^{57}Fe in several metal hosts agrees with that derived from the susceptibility measurements in Ref. 2.

The hyperfine field at the ^{57}Fe nucleus is related to the properties of the host and its interactions with the ^{57}Fe and yields information about the microscopic magnetization. In fact the nucleus feels an effective magnetic field $H_{\rm eff}$ which is given by the sum of the external field $H_{\rm ext}$ and the induced hyperfine field $H_{\rm hf}$, *i.e.*, $H_{\rm eff}=H_{\rm ext}+H_{\rm hf}$. The magnitude of $H_{\rm hf}$ is assumed to be proportional to the electronic polarization localized on the impurity site.

In general, $H_{\rm hf}$ involves a dominant temperature-dependent term and a small temperature-independent term. Hence $H_{\rm hf}$ is expressed as

$$H_{\rm hf}=H_{\rm loc}(H_{\rm ext},T)+\beta H_{\rm ext}, \tag{11}$$

where $H_{\rm loc}$ denotes the contribution of local d-spin moment, and the second term expresses the field-induced Van Vleck paramagnetism of higher lying electronic states. The parameter β is a constant which can be determined experimentally.

If the impurity has a well-defined magnetic moment $\mu=g\mu_{\rm B}S$ and the electronic relaxation times are much shorter than the Larmor precession time of the nucleus in $H_{\rm eff}$, then we may write

$$H_{\rm hf}=H_{\rm sat}<S_z>/S, \tag{12}$$

where $<S_z>$ is the time average of S in the direction of $H_{\rm ext}$, and $H_{\rm sat}$ is the value of $H_{\rm hf}$ when $<S_z>=S$. For a free paramagnetic spin, this expression becomes

$$H_{\rm hf}=H_{\rm sat}B_s(\mu H_{\rm ext}/kT), \tag{13}$$

where $B_s(x)$ is the Brillouin function. Several attempts have been made to modify Eq. (13) phenomenologically in order to account for the low-temperature Kondo-effect deviations.[27,28]

Unfortunately, at the present stage, no appropriate theory exists, predicting the behavior of $H_{\rm hf}$ based on the LSF concept. Nevertheless, using a simple stochastic model, we attempt a qualitative prediction of $H_{\rm hf}$ in LSF systems. For simplicity, we assume that a magnitude of the temporary spin at the Fe impurity is 1/2 and that it decays with a characteristic lifetime of $\tau_{\rm sf}=h/kT_{\rm sf}$ at temperature below $T_{\rm sf}$. In an external field $H_{\rm ext}$, due to the electronic Zeeman splitting, the energy level of the down spin state becomes lower than the up spin state by $g\mu_{\rm B}H_{\rm ext}$. Hence the probability that the temporary spin stays in the down state $P(\downarrow)$ is larger than that of the up state $P(\uparrow)$.

In the Mössbauer experiment, $H_{\rm hf}$ appears as a time-averaged value during the Larmor precession period $\tau_{\rm L}$. For example, the effective magnetic field of 50 kOe corresponds to $\tau_{\rm L}=2.5\times10^{-7}$ sec for ^{57}Fe nucleus. This value is much larger than $\tau_{\rm sf}(=5\times10^{-13}$ sec for $T_{\rm sf}=100$ K) and permits to express $H_{\rm hf}$ by

$$H_{\rm hf}=-<P(\downarrow)|H\uparrow|-P(\uparrow)|H\uparrow|>, \tag{14}$$

where $H\downarrow$ and $H\uparrow$ represent the hyperfine field for the down spin state and the up spin state, respectively. The bracket means a time average during $\tau_{\rm L}$.

Since $P(\downarrow)$ and $P(\uparrow)$ do not obey the Boltzmann distribution, it is not possible

to express them by a simple analytical form. The reason for this is that at temperatures well below T_{sf} and in a high external field, the thermal relaxation time becomes larger than τ_{sf}, and consequently a temporary spin does not have time to come into thermal equilibrium before vanishing. In this case, one may expect that the probability ratio $P(\uparrow)/P(\downarrow)$ has a larger value than that in the thermal equilibrium. In addition, since the temporary spin decays with a lifetime τ_{sf}, the probability for the spin absence is not zero, *i.e.*, $P(\uparrow)+P(\downarrow)<1$. This is essentially different from the usual relaxation phenomenon of permanent spins.

Enhancement of the ratio $P(\uparrow)/P(\downarrow)$ and a certain finite value of the probability for spin zero would give rise to that the difference between $P(\downarrow)$ and $P(\uparrow)$ be much smaller than unity, *i.e.*, $P(\downarrow)-P(\uparrow)\ll 1$. Besides, if $|H\downarrow|$ and $|H\uparrow|$ are presumed to be almost equal, from Eq. (14), one can reasonably expect an unusually small hyperfine field in LSF systems at temperatures much below T_{sf}.

III. EXPERIMENTAL

1. Measurements of T_0

Using metallic Tc samples containing dilute Mn, Fe, and Co impurities, we measured the superconducting transition temperature T_0. Since the details of sample preparations and of the measurements have been reported in our previous papers,[10,29] only the essence is reviewed here.

Technetium and 3d impurities (Mn, Fe, Co) were electrolytically deposited on a thin nichrome film. In each sample, tracer amount of ^{54}Mn, ^{55}Fe, and ^{57}Co was simultaneously deposited. Thus the total amounts of ^{99}Tc and the impurity recovered from the electrolyte were radioactively determined. The sample thicknesses are 8–9 μm and the maximum impurity concentration is 0.25 at.%. These samples were heat-treated in pure hydrogen atmosphere at 1000°C for 4 h. The transition temperature was determined by measuring the ac resistance as a function of temperature, where the conventional ac four-probe technique was employed.

As described in Sec. II, the initial depression of T_0 is an important measure of the magnetic character of the impurity involved. Our measurements gave that $-(dT_0/dn)_{n\to 0}=0.6$, 2.9, and 1.2 K/at.% for Mn, Fe, and Co, respectively. In Fig. 1 are plotted the values of the initial depression of T_0 of Tc,[10,30] Ru,[8,31] and Ir[9] by 3d magnetic impurities against atomic number of the impurities.

2. Measurements of H_{hf}

In the present experiment, three kinds of samples were prepared and they were used as the Mössbauer sources.

TcFe: Tc was first electrodeposited on a Cu plate. Then carrier-free ^{57}Co (0.12 μg/mCi) and Tc were simultaneously electrodeposited, of which the total thickness was about 10 μm. Reduction and annealing of the sample were carried out in a flowing pure hydrogen atmosphere. X-ray analysis confirmed the presence of metallic Tc having the characteristic hcp structure.

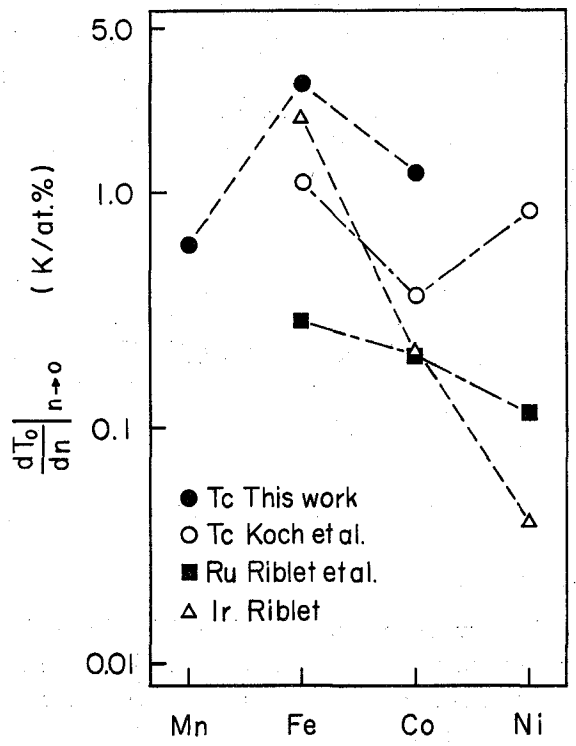

Fig. 1. The initial depression of T_0 for Tc, Ru, Ir–3d impurity alloys, plotted against the atomic number of the impurity. Data of Koch *et al.* are from Ref. 30, Riblet *et al.* from Refs. 8 and 31, and Riblet from Ref. 9.

RuFe: A pressed flat disk of 200-mesh powder was used as the Ru host. On the disk, a proper amount of liquid ^{57}Co solution was deposited and then the disk was heat-treated in the hydrogen atmosphere, and in a high vacuum.

IrFe: An Ir foil of 50 μm was used as the Ir host. A proper amount of ^{57}Co solution was dried onto the foil and it was heat-treated in the hydrogen atmosphere. Specific information on the preparation of all samples are listed in Table I.

Table I. Specifications for Sample Preparation

Host	Shape	Thickness (μm)	^{57}Co (μCi)	Annealing
Tc (hcp)	Electrodeposited foil	10	35	900°C 46 h in H_2
Ru (hcp)	Pressed disk	500	400	1100°C 6 h in H_2
				1050°C 10 h in vacuum
Ir (fcc)	Foil	50	100	1100°C 25 h in H_2

The Mössbauer measurement was performed in the temperature region of 1.4–290 K and in the external magnetic field H_{ext} up to 50 kOe. The spectra were obtained in the standard transmission geometry with a fixed source and a moving room-temperature absorber. External magnetic field was produced using a superconducting solenoid, in which the axis of the field was perpendicular to the sample surface and was parallel to the γ-ray direction. A GaAs Hall probe was used for calibrations of field strength within an error of $\pm$0.5 kOe. Temperature was measured by the vapor pressure of ^{4}He at 1.4–4.2 K and by a thermocouple of Au–0.07 at.%Fe vs. Ag–0.37 at.%Au above 4.2 K.

A single line absorber of potassium ferrocyanide containing 0.5 or 1.0 mg/cm^2 of ^{57}Fe was always kept at room temperature. A fringing field acting on the absorber is less than 5% of the field at the solenoid center. The calibration of the velocity was made by the known magnetic splitting of α–Fe.

It is well known that in hcp transition metals there is an electronic field gradient resulting in appearance of a quadrupole splitting (QS). In our previous paper,[14] the QS of ^{57}Fe impurity in Tc was determined as -0.13 ± 0.02 mm/sec. For the Ru (hcp) host, by a similar analysis of the spectrum at room temperature, we determined the absolute value of QS as 0.14 ± 0.02 mm/sec, which is in excellent agreement with that by Wortmann and Williamson.[32] Since the values of QS for both Tc and Ru are sufficiently small, we analyzed the hyperfine spectra by assuming a Lorentzian

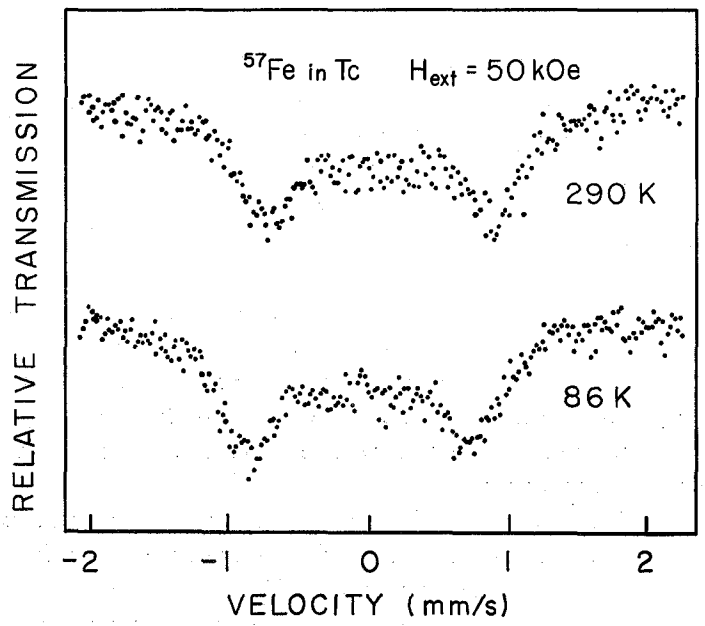

Fig. 2. Mössbauer spectra with a source of ^{57}Fe in Tc in external field of 50 kOe at 290 and 86 K. A single line absorber of pottasium ferrocyanide containing 1.0 mg/cm^2 of ^{57}Fe was used at room temperature. The γ-ray direction is parallel to the external field.

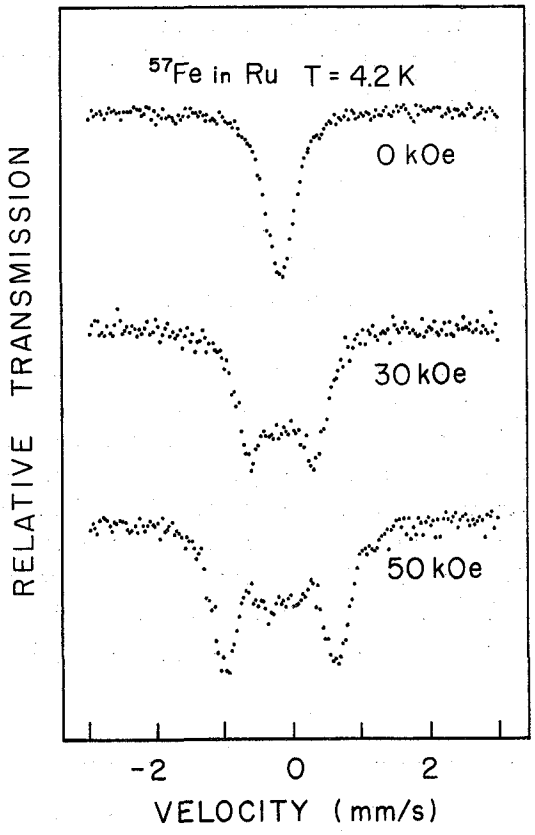

Fig. 3. Mössbauer spectra with a source of ^{57}Fe in Ru at 4.2 K for various external fields. The absorber is potassium ferrocyanide containing 0.5 mg/cm^2 of ^{57}Fe.

line shape, the ideal intensity ratio of 3: 0: 1: 1: 0: 3, and equal line widths. Observed spectra with Tc and Ru are shown in Figs. 2 and 3.

For the Ir (fcc) sample, which has no quadrupole interaction, the spectra at 290 and 86 K were well fitted by the above functional form. However, below 4.2 K, the spectra showed an anomalous contribution of the inner part of spectra (see Fig. 4). Nevertheless, $H_{\rm eff}$ was determined within an error of ± 1 kOe from the splitting of the outer pair of lines, which were well resolved and unaffected by the anomalous growth at the central part of the spectra.

In Figs. 5 and 6, $H_{\rm hf}$ at ^{57}Fe nucleus in Tc, Ir, and Ru is plotted as a function of $H_{\rm ext}/T$. The solid and broken lines in the figures are drawn only for seeing easily and do not represent any theoretical prediction. The parameter β in Eq. (11), which indicates the contribution of Van Vleck paramagnetism, was estimated by plotting the observed values of $H_{\rm hf}/H_{\rm ext}$ as a function of $1/T$, and then by extrapolating the curve to $1/T \to 0$. The value thus obtained is zero within experimental error for TcFe, and -0.02 ± 0.01 for IrFe. Because of the smallness of β, $H_{\rm hf}$ can be con-

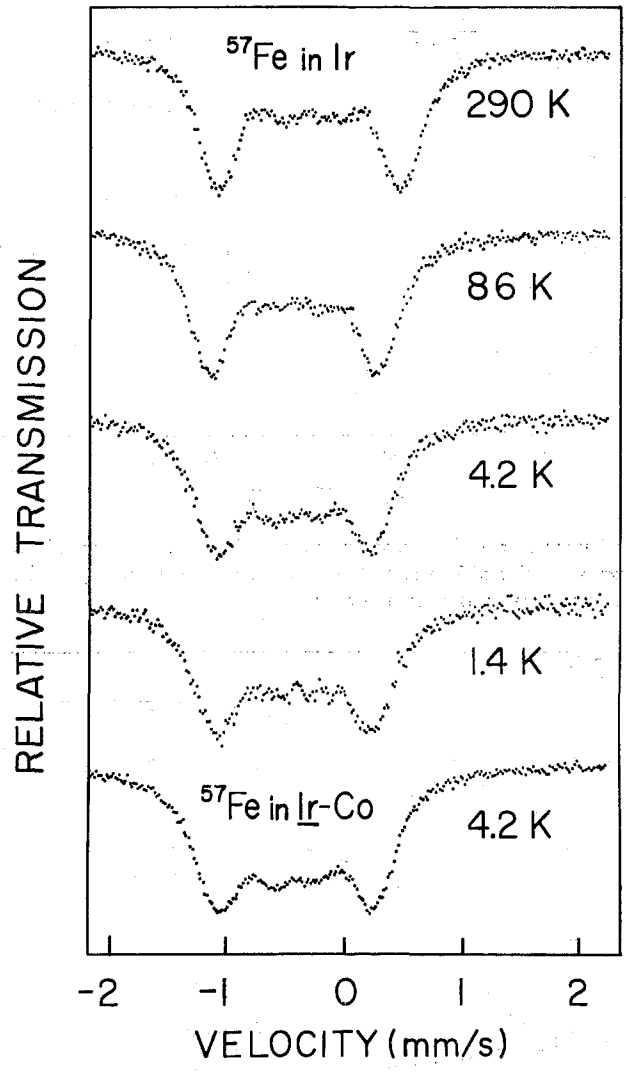

Fig. 4. Mössbauer spectra with a source of ^{57}Fe in Ir in external field of 50 kOe at various temperatures. The bottom spectrum is obtained with a source of ^{57}Fe in IrCo (see text).

sidered to be proportional to the 3d magnetization on Fe impurity site.

As seen in the figures, the saturation values of H_{hf} in H_{ext}=50 kOe are $-7.3\pm$ 1 kOe for TcFe and -9.3 ± 1 kOe for IrFe. The latter result is in agreement with the previous work.[13]

As shown in Fig. 6, all of the values of H_{hf} for RuFe are so small ($|H_{hf}|<2$ kOe) and lack of definite dependence on T and H_{ext}.

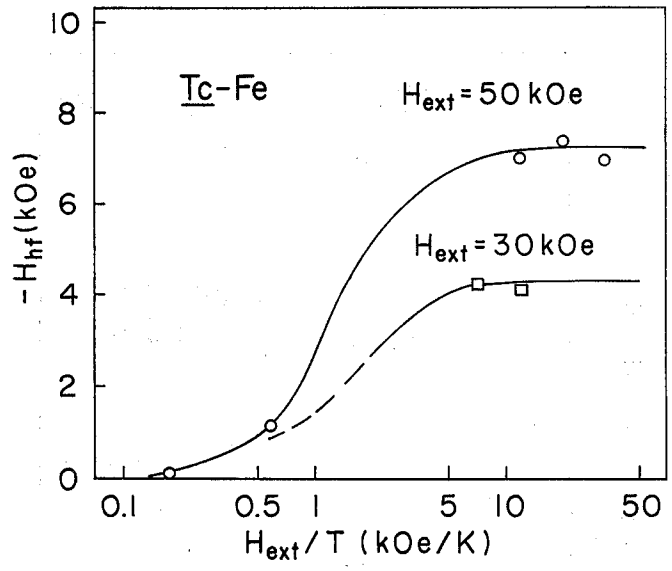

Fig. 5. Behavior of the ^{57}Fe hyperfine field in Tc as a function of H_{ext}/T at external fields of 30 and 50 kOe. The standard error is ± 1 kOe. Solid lines are drawn as a visual aid only.

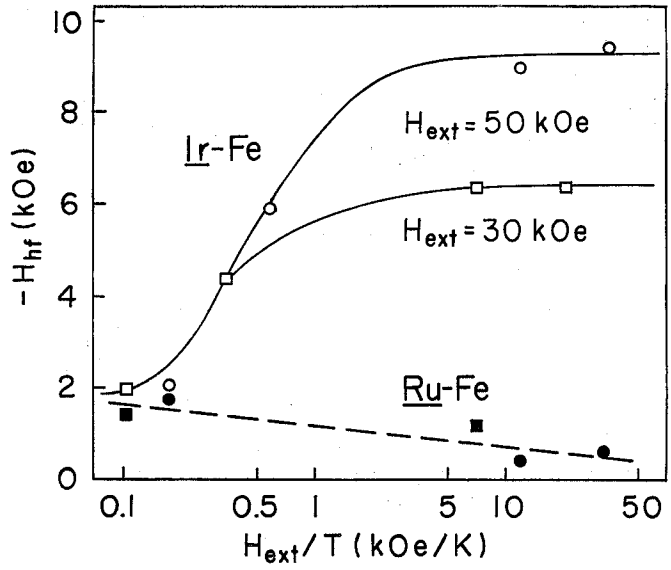

Fig. 6. Behavior of the ^{57}Fe hyperfine field in Ir and Ru as a function of H_{ext}/T. Data are taken at $H_{ext}=50$ kOe (○: Ir, ●: Ru) and $H_{ext}=30$ kOe (□: Ir, ■: Ru). The standard error is ± 1 kOe.

IV. DISCUSSION

As shown in Fig. 1, the initial decrease in T_0 with respect to impurity concentration apparently depends on the property of impurities. In the case of Tc host,

our results show that the Fe impurity suppresses T_0 more intensely than Mn and Co. This suggests that the magnetic nature of Fe has a responsibility for the observed rapid suppression of T_0. This tendency is, as seen in the figure, consistent with other works with Tc, Ru, and Ir hosts.

As mentioned before, in both RuFe and IrFe systems, the presence of LSF has been revealed by the measurements of resistivity and transition temperature. Besides, the relative strength of the impurity effect is most intensive for Fe. This result differs from the case of simple metal host like Al–3d[33] and Zn–3d[34] systems, where $-(\mathrm{d}T_0/\mathrm{d}n)_{n\to 0}$ has the maximum at Mn impurity. In the case of simple metal hosts, the magnetic properties of 3d impurities is closely related to the electronic spin alignment predicted by the Hunt's rule. According to the rule, the magnitude of the electronic spin of 3d impurity series has the maximum value of 5/2 at Mn, and thus the magnetic property of Mn should be stronger than others. The rather complex behavior in Fig. 1 for Tc, Ru, and Ir hosts may be due to the facts that these systems consist of transition metals both as host and impurity, and that the valence difference is small between the host and impurity.

The theoretical prediction of the change in $T_0(n)$ for rapid spin fluctuation systems is given by Eq. (3). This formula gives a linear or slightly downward curves of $\ln[T_0(n)/T_{c0}]$. Our previously reported result[10] of TcFe is consistent with this prediction, suggesting that TcFe is a LSF system. Unfortunately, since our data of $T_0(n)$ are limited to low concentrations, it is difficult to estimate the parameters A and B in Eq. (3) independently, and to estimate the spin fluctuation temperature from Eq. (6).

In order to compensate for the limited available information on LSF systems, the measurements of hyperfine field $H_{\mathrm{hf}}(H_{\mathrm{ext}}, T)$, which reflects the dependence of the local magnetization on magnetic fields and on temperature, have been made. It is remarkable that the saturation values of H_{hf} of TcFe, RuFe, and IrFe are much smaller than those found for usual Kondo systems under a similar experimental condition (*e.g.*, -110 kOe for MoFe[35]). These results are well explained qualitatively by the theoretical approach developed in this paper. The curves of H_{hf} observed here are not a unique function of H_{ext}/T, and the saturation values of H_{hf} are almost proportional to the magnitude of H_{ext}. At any rate, the close similarity in both the magnitude and behavior of H_{hf} between TcFe and IrFe suggests that the spin fluctuation temperature of TcFe has the same order of magnitude as IrFe. This is supported by the fact that the initial depression of T_0 for TcFe is comparable to that of IrFe. For IrFe, the present result is consistent with the bulk susceptibility measurement of dilute Fe impurities in Ir by Knapp,[36] who has indicated that the magnetization does not saturate, but is practically linear with H_{ext} between 0.37–293 K under H_{ext} up to 11 kOe.

The field dependence of H_{hf} of TcFe and IrFe systems closely resembles the behavior in such Kondo systems as CuFe[37,38] and RhFe[39] under the condition of $\mu H_{\mathrm{ext}} < kT_{\mathrm{K}}$, where μ is the magnitude of the local moment and T_{K} is the Kondo temperature. In these Kondo systems, the proportionality between the saturated value of H_{hf} and H_{ext} is interpreted as the evidence for the growth of the magnetic

moment due to the gradual breading up of the spin-compensated Kondo state by the external field. On the other hand, according to our theoretical approach in Sec. II, the proportionality between H_{hf} and H_{ext} is reduced to the proportionality between $[P(\downarrow)-P(\uparrow)]$ and H_{ext}, because $|H\downarrow|$ and $|H\uparrow|$ are presumed to be almost equal. Taking into account the fact that the spin does not obey the Boltzmann distribution, the proportionality between $[P(\downarrow)-P(\uparrow)]$ and H_{ext} is not unlikely.

Estimations of the saturation hyperfine field H_{sat} of Kondo systems (CuFe, RhFe) are made by assuming that the data at temperatures much higher than T_K are represented by the Brillouin function. In the present TcFe and IrFe cases, however, a similar analysis is not applicable for the following reason: Based on the assumption that T_{sf} of LSF systems is equivalent to T_K of Kondo systems, as suggested by Rivier and Zuckermann,[40] the experimental temperature should be much higher than T_{sf} for proper estimation of H_{sat}. But the maximum temperature in our experiment is 290 K. Besides H_{hf} is so small that the field dependence of H_{hf} can not be determined for a Brillouin function.

As to RuFe, negative H_{hf} can be interpreted as the result that the contribution of the negative 3d magnetization exceeds the positive Van Vleck contribution. In particular, the lack of a strong temperature dependence of H_{hf} below room temperature permits us to say that the spin fluctuation temperature is in much excess of 290 K. This is in general agreement with the result inferred by Kao and Williams[7] ($T_{sf}>$ 700 K) from an analysis of the temperature dependence of the electrical resistivity. Furthermore, the small H_{hf} of RuFe is consistent with the fact that the depression of T_0 of RuFe is much smaller than that of TcFe and of IrFe (see Fig. 1).

We turn to the Mössbauer spectra of the IrFe sample (Fig. 4). The spectra at low temperature (4.2 and 1.4 K) in 50 kOe have an additional amplitude in the inner part compared with the spectra at 290 and 86 K. After various attempts, it was found that these spectra were well fitted by a computer analysis with the ratio of 3: 0: α: α: 0: 3 and using a single line width. Thus the value of α was determined as 1.4 and 1.2 at 4.2 and 1.4 K, respectively. The line width at 4.2 and 1.4 K was larger than that at 290 K by 12% and 17%, respectively. However, under $H_{ext}=0$, there is no appreciable broadening of line width (compared with that at 290 K), indicating that no spontaneous magnetic ordering occurs down to 1.4 K. Similar anomalous spectra of MoFe[26,35,41] and RhFe[42] have been reported, but in the previous paper with IrFe by Taylor and Steyert,[13] there is no description about such an anomaly.

There are two possible explanations of this enhanced amplitude in the inner part of the spectra. A simple explanation is a distribution of the hyperfine field due to inhomogeneities in the sample. In other words, the spectrum is a superposition of several peaks corresponding to different magnitudes of H_{hf}, which is caused by an interaction between impurities or by clustering of the impurities. Another explanation is, as proposed by several authors on MoFe[35,41] and RhFe,[42] the presence of relaxation effects which generally occur when the electronic relaxation time becomes comparable with the Larmor precession time of ^{57}Fe nucleus in the effective hyperfine field.

In order to inquire into the cause of the anomaly, another Ir sample containing

0.35 at.% Co impurities was prepared by means of the simultaneous electrodeposition of 1 mCi ^{57}Co with non-active Co. The diffusion treatment was the same as that used for the "pure" Ir sample. The local concentration of Co near the surface is expected to be more than 0.5 at.%. As shown in the lowest part of Fig. 4, the spectrum at 4.2 K and 50 kOe of this sample does not show any essential difference from that of the sample containing only carrier free ^{57}Co. This result means that the anomaly in the IrFe spectrum is not caused by clustering of Co atoms in the sample, and relaxation phenomena, it is necessary to know the initial population of the electronic system. However, for LSF systems, $P(\downarrow)$ and $P(\uparrow)$ are not represented by the Boltzmann distribution, as discussed before. This makes very difficult to obtain the spectrum by a model including the relaxation effect. Further theoretical work is needed to get more definite conclusion on the anomalous Mössbauer spectrum observed for IrFe.

ACKNOWLEDGMENTS

The authors wish to express their thanks to T. Ishida and N. Hosoito for their assistance in the measurement. Kind arrangements for sample preparations in the Radioisotope Research Center of our University are also acknowledged.

REFERENCES

(1) B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, *Phys. Rev. Lett.*, **5**, 542 (1960).
(2) A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.*, **125**, 541 (1962).
(3) P. W. Anderson, *Phys. Rev.*, **124**, 41 (1961).
(4) T. H. Geballe, B. T. Matthias, A. M. Clogston, H. J. Williams, R. C. Sherwood, and J. P. Maita, *J. Appl. Phys.*, **37**, 1181 (1966).
(5) See for example, D. L. Mills, M. T. Béal-Monod, and P. Lederer, "Magnetism," Vol. V, ed. by H. Suhl, Academic Press, New York, (1973), Chapter 3.
(6) N. Rivier and V. Zlatic, *J. Phys. F* **2**, L99 (1972).
(7) F. C. C. Kao and G. Williams, *J. Phys. F* **4**, 419 (1974).
(8) G. Riblet, R. Schmidt, and H. von Löhneysen, *Solid State Comm.*, **26**, 53 (1978).
(9) G. Riblet, *Phys. Rev. B* **3**, 91 (1971).
(10) T. Takabatake and H. Mazaki, *Phys. Rev. B* **19**, 189 (1979).
(11) T. A. Kitchens and R. D. Taylor, *Phys. Rev. B* **9**, 344 (1974).
(12) J. G. Pérez-Ramírez and P. Steiner, *J. Phys. F* **7**, 1573 (1977).
(13) R. D. Taylor and W. A. Steyert, *J. Appl. Phys.*, **37**, 1336 (1966).
(14) T. Takabatake, H. Mazaki, and T. Shinjo, *Phys. Rev. Lett.*, **40**, 1051 (1978).
(15) W. Buckel and R. Hilsch, *Z. Phys.*, **128**, 324 (1950).
(16) B. T. Matthias, *IBM J. Res. Develop.*, **6**, 250 (1962).
(17) A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksp. Teor. Fiz.*, **39**, 1781 (1960); English Transl. *Soviet Phys. JETP*, **12**, 1243 (1961).
(18) J. Friedel, *Nuovo Cimento Suppl.*, **7**, 287 (1958).
(19) A. B. Kaiser, *J. Phys. C* **3**, 410 (1970).
(20) J. G. Huber and M. B. Maple, *J. Low Temp. Phys.*, **3**, 537 (1970).
(21) M. B. Maple, "Magnetism," Vol. V, ed. by. H. Suhl, Academic Press, New York, (1973), Chapter 10.

(22) W. L. McMillan, *Phys. Rev.*, **167**, 331 (1968).
(23) J. Rössler and M. Kiwi, *Phys. Rev. B* **10**, 95 (1974).
(24) M. Kiwi and J. Rössler, *Solid State Comm.*, **15**, 1581 (1974).
(25) M. J. Zuckermann, *J. Phys. C* **3**, 2130 (1970).
(26) T. A. Kitchens, W. A. Steyert, and R. D. Taylor, *Phys. Rev.*, **138**, A467 (1965).
(27) W. Götze and P. Schlottmann, *J. Low Temp. Phys.*, **16**, 87 (1974).
(28) K. D. Schotte and U. Schotte, *Phys. Lett.*, **55A**, 38 (1975).
(29) M. Kurakado, T. Takabatake, and H. Mazaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**, 38 (1977).
(30) C. C. Koch, W. E. Gardner, and M. J. Mortimer, "Low Temperature Physics-LT13," Vol. 2, ed. by K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel, Plenum Press, New York, (1974), p. 595.
(31) G. Riblet and M. A. Jensen, *Physica*, **55**, 622 (1971).
(32) G. Wortmann and D. L. Williamson, *Hyperfine Int.*, **1**, 167 (1975).
(33) E. Babić, P. J. Ford, C. Rizzuto, and E. Salamoni, *J. Low Temp. Phys.*, **8**, 219 (1972).
(34) G. Boato, G. Gallinaro, and C. Rizzuto, *Phys. Rev.*, **148**, 353 (1966).
(35) M. P. Maley and R. D. Taylor, *Phys. Rev. B* **1**, 4213 (1970).
(36) G. S. Knapp, *J. Appl. Phys.*, **38**, 1267 (1967).
(37) R. B. Frankel, N. A. Blum, B. B. Schwartz, and D. J. Kim, *Phys. Rev. Lett.*, **18**, 1051 (1967).
(38) P. Steiner, S. Hüfner, and W. v. Zdrojewski, *Phys. Rev. B* **10**, 4704 (1974).
(39) P. E. Clark, *Solid State Comm.*, **12**, 469 (1973).
(40) N. Rivier and M. J. Zuckermann, *Phys. Rev. Lett.*, **21**, 904 (1968).
(41) H. Maletta, K. R. P. M. Rao, and I. Nowik, *Z. Phys.*, **249**, 189 (1972).
(42) B. Window, W. T. Oosterhuis, and G. Longworth, *Int. J. Magnetism*, **6**, 93 (1974).