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Experimental Study of the Host NMR Linewidth and Spin-Lattice Relaxation Rate in Dilute *Cu*Fe Alloys below the Kondo Temperature[*]

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In order to determine the properties of single magnetic impurities in the Kondo state and the effects of these single magnetic impurities on the host-conduction-electron spin system, the Fe-impurity contributions to the Cu^{63}-host nuclear-magnetic-resonance (NMR) linewidth ΔH_i, and spin-lattice relaxation time T_{1i}, have been studied over a wide Fe-concentration range ($0<c<1260$ ppm) in *Cu*Fe. The NMR-linewidth measurements made from 1.65 to 77 °K and in magnetic fields from 2 to 16 kOe and in some cases up to 60 kOe, show the anomalous behavior of the slope $S=d\Delta H_i/dH$ originally observed by Heeger *et al.* and studied for a 480-ppm *Cu*Fe alloy by Golibersuch and Heeger exists over a wide Fe-concentration range. This anomalous behavior, which consists of the transition from a constant slope at low fields, S_L, to a smaller magnitude slope at high fields, S_H, occurs in a relatively narrow range of fields about some critical field H_c. This behavior clearly results from the single-impurity contribution to the NMR linewidth as evidenced by the linear concentration dependence of both S_L and S_H and also by the concentration independence of S_L/S_H. S_H has the same $(T+29)^{-1}$ temperature dependence as the bulk susceptibility, while S_L is enhanced for $H<H_c$ and $T<T_c\approx 6$ °K. At 1.65 °K, $S_H=(1.50\pm0.10)\times10^{-6}c$, $S_L=(2.83\pm0.10)\times10^{-6}c$ (c in ppm), and $S_L/S_H=1.9$. These results show that the Ruderman-Kittel-Kasuya-Yosida-like oscillatory conduction-electron spin polarization existing about an impurity for $T\gg T_K$ is either enhanced for $T<T_c$ and $H<H_c$, or else an additional long-range oscillatory spin polarization is formed in the Kondo state. From the inverse concentration dependence of H_c we conclude that long-range interactions of sufficient strength exist between Fe spins via the d-d double-resonance mechanism to effectively saturate the extra oscillatory spin polarization in successively smaller applied fields as the Fe concentration increases. The impurity-induced host relaxation rate is linear in Fe concentration up to at least 300 ppm, decreasing from $T_{1i}^{-1}=2.3\times10^{-3}c$ (c in ppm) for 2.65 kOe to $T_{1i}^{-1}=2.5\times10^{-4}c$ for 15 kOe at 1.65 °K. The low-concentration data follow a single curve when plotted as $T(cT_{1i})^{-1}$ vs T/H (0.1 °K/kOe $<T/H<1.0$ °K/kOe). Comparison of this curve with the existing high-temperature ($T\gg T_K$) theories would imply that the spin-lattice relaxation in the liquid-helium temperature range is dominated by a dipolar coupling of the nuclei to longitudinal dipolar fluctuations of the impurity spin. These results are discussed in the light of the T_{1i} data for $T>T_K$ which does not appear to be consistent with this mechanism suggesting that none of the $T\gg T_K$ relaxation mechanisms may be simply extended to the region $T<T_K$.

I. INTRODUCTION

Dilute alloys of magnetic impurities in a nonmagnetic host metal have for several years been the subject of considerable experimental and theoretical investigation.[1] The nature of the ground state or Kondo state of the magnetic impurity and the form of the correlations between the impurity d spin and nearby host-conduction-electron spins for temperatures below the Kondo temperature T_K have been of particular interest. The host nuclear magnetic resonance (NMR) has proved to be a particularly useful probe for determining the effects of the impurities upon the host-conduction-electron system, because the impurity spin induces a Ruderman-Kittel-Kasuya-Yosida (RKKY)-type spin polarization in the conduction-electron system which is sensed by the host nuclei via the contact interaction ($A\vec{I}\cdot\vec{\sigma}$). Information about the magnitude and form of the oscillatory spin polarization may then be obtained by observing the field and temperature dependence of the host NMR properties.

Several detailed investigations of the effect of magnetic impurities on the host NMR properties below T_K have been performed in recent years. Following the original study by Sugawara[2] at liquid-helium temperatures, Heeger *et al.*[3] determined the impurity contribution to the host NMR linewidth ΔH_i in *Cu*Fe and *Cu*Cr from 0.5 to 0.03 °K. The latter group found ΔH_i for *Cu*Fe and *Cu*Ce to have a value much smaller than that which would have been expected from the high-temperature measurements indicating, along with susceptibility data, that the Kondo state was nonmagnetic. A very interesting feature of the data of Heeger *et al.* was an anomalous change in the slope $d\Delta H_i/dH$ with increasing applied field for *Cu*Fe (an apparent change by a factor of 2.5 at 20 kOe when combined with the Mössbauer data for $H > 20$ kOe) and *Cu*Cr (a factor of 4 change at 2.5 kOe). However, Heeger *et al.* studied this anomaly in just one sample each of *Cu*Fe and *Cu*Cr.

The temperature dependence of this anomalous behavior of the Cu-host NMR linewidth was then studied in detail by Golibersuch and Heeger[4] at applied fields less than 12 kOe on a 480-ppm *Cu*Fe sample. They found the slope $d\Delta H_i/dH$ appeared to scale with the bulk susceptibility data[5] and varied as $(T+30)^{-1}$ for $T > 20$ °K, but increased faster than $(T+30)^{-1}$ below 20 °K. They took the differences between their data and an extrapolated $(T+30)^{-1}$ fit to represent the intrinsic temperature dependence of the "quasiparticle-spin-polarization cloud" surrounding the Fe impurity in the Kondo state. They obtained a similar profile of the field dependence of this enhancement from the ΔH_i vs H plot of Heeger *et al.* by assuming that the high-field slope resulted from the simple perturbative RKKY spin polarization. However, the more recent bulk-magnetization measurements of Tholence and Tournier[6] led to the speculation that this behavior could be attributed to Fe pairs. They found the single-impurity contribution to the bulk susceptibility varied as $(T+29)^{-1}$ at all temperatures, and suggested any deviations from this behavior resulted from the saturation of nearly magnetic Fe pairs.

In this paper we present a study of the Cu^{63} NMR linewidth and spin-lattice relaxation rate in order to determine the *single-impurity* behavior of Fe impurities in dilute *Cu*Fe alloys below T_K. Linewidth measurements have been made over a wide range of Fe concentrations ($0 < c < 1260$ ppm), applied fields ($2 < H < 60$ kOe), and temperatures ($1.65 < T < 77$ °K), and the spin-lattice relaxation rate has been measured as a function of applied field ($2.5 < H < 16$ kOe) and temperature ($1.4 < T < 4.2$ °K) for the same samples. Some aspects of this work have been published in preliminary reports.[7,8]

Our results clearly show that the host-linewidth anomaly observed in *Cu*Fe results from the *single-impurity* behavior of an Fe impurity, and it is a consequence of either the enhancement of the RKKY-type polarization induced by the magnetic impurity in the Kondo state or else the formation of an additional long-range oscillatory spin polarization below T_K which has a spatial dependence differing from the RKKY-type term. The Cu spin-lattice relaxation rate is also enhanced at liquid-helium temperatures with a field- and temperature-dependent best fit by the longitudinal dipolar relaxation mechanism although it is not clear that this can account for the relaxation rate at higher temperatures.

In Sec. II we present details of our experimental techniques. The results of the Cu NMR linewidth and spin-lattice relaxation rate measurements in *Cu*Fe are presented in Sec. III. A discussion of the more important features of the data appears in Sec. IV, and our principal conclusions will be summarized in Sec. V.

II. EXPERIMENTAL DETAILS

The samples used in this study were prepared from 99.999% pure copper (Marz grade from Materials Research Corp., Orangeburg, New York). Two grades of iron wire used: 99.9% pure (Allied Chemical; Morristown, New Jersey) and 99.999% pure (Marz grade from Materials Research Corp.). The starting constituents were sealed in a quartz tube under a partial atmosphere of high-purity argon gas, melted in an induction furnace and held at 1200 (±20) °C for 100 min. Some of the samples were annealed at 800–900 °C for 100 h and then rapidly quenched in cold water, while other samples received no anneal. No variations in the NMR properties were found to result either from the grade of Fe used or any differences in the heat treatments of the samples.

The samples were characterized by absorption spectroscopy to an estimated accuracy of ±10 ppm for all samples except the 1260-ppm sample which was ±30 ppm. As a check on the sample-preparation procedures, a 750-ppm sample was prepared by melting in an argon arc furnace with a water-cooled copper hearth (which produced a much more rapid quench than could be obtained in the induction furnace). No variations in the Cu^{63} NMR properties of this sample could be observed when compared against samples prepared using the induction furnace. Filings obtained from opposite ends of a sample ingot yielded identical NMR linewidths, and the chemical analysis from these two ends was identical within ±10 ppm, indicating a high degree of homogeneity throughout the sample volume. An analysis for other transition-metal impurities showed their total concentration to be less than about 5 ppm. The samples were comminuted by mechanical filing using a fine-cut tungsten-carbide file and then passed through a 325-mesh sieve.

Linewidth measurements were made using a marginal oscillator in a continuous wave (cw) NMR spectrometer of conventional design. The high-field measurements ($H > 16$ kOe) were made in a compensated 0–75-kOe Nb-Ti superconducting solenoid. For the most concentrated *Cu*Fe samples, we observed peak-to-peak linewidths for the derivature of the Cu NMR absorption line as large as 50 Oe. The small signal-to-noise ratio for these samples required electronic signal averaging. Regulation of the sample temperature to within ±0.2 °K at 6 °K and ±1 °K at 30 °K was achieved with an automatic temperature controller.

The spin-lattice relaxation-time measurements were made using a phase-coherent single-coil pulsed NMR spectrometer. In some cases the Cu^{63} echo was electronically averaged, using a Fabritek 1072 instrument computer with a 1-μsec/channel resolution. A comb of pulses was applied at the resonance frequency in order to saturate the Cu resonance. This comb was followed after a time t by a φ-τ-φ pulse sequence, where $\varphi \simeq 90°$. The length and intensity of the saturating comb was determined by the width of the resonance line; typical combs consisted of 250- to 400 20-μsec pulses spaced 1 msec apart. The repetition rates were kept lower than $(7T_1)^{-1}$ at all times to ensure that the nuclei had completely relaxed to thermal equilibrium before beginning another sampling.

III. EXPERIMENTAL RESULTS

A. Cu^{63} Host Linewidth

In this section we present the experimental results for the inhomogeneous broadening of the Cu^{63} NMR linewidth by dilute concentrations of Fe impurities. Linewidths reported here represent the peak-to-peak width of the derivative of the absorption curve. The measurements have been made in magnetic fields from 2 to 16 kOe and in some cases up to 60 kOe, from 1.65 to 77 °K, for Fe concentrations from 90 to 1260 ppm.

In Fig. 1 we show examples of the measured Cu^{63} NMR linewidth ΔH vs applied magnetic field for a number of samples from 90 to 1165 ppm at 1.65 °K. The measurements for the higher-concentration samples were not extended to the highest fields as a result of insufficient signal-to-noise ratio. Note that in Fig. 1 the measured linewidths clearly show that the broadening of the Cu line is not linear in field, but increases more slowly at higher fields. The fact that ΔH does not extrapolate to the pure-Cu value of $\Delta H = 6.35 \pm 0.20$ Oe at zero field has been attributed alternately to the existence of Fe

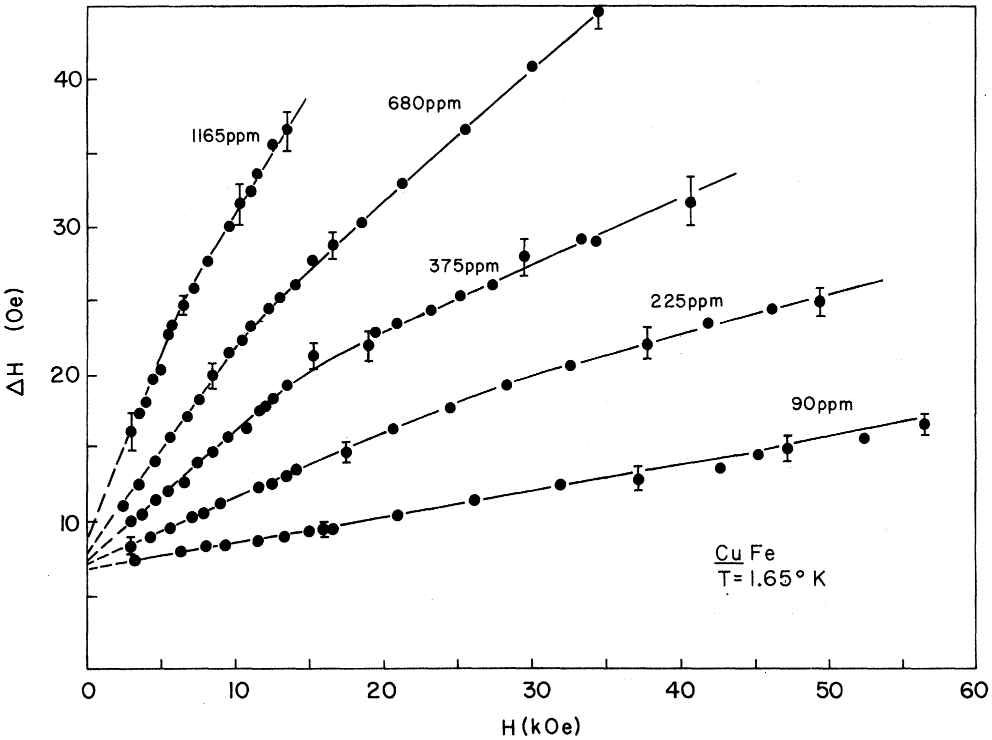

FIG. 1. Magnetic field dependence of the measured Cu^{63} (peak-to-peak) NMR linewidth at 1.65 °K for representative samples with Fe concentrations of 90, 225, 375, 680, and 1165 ppm.

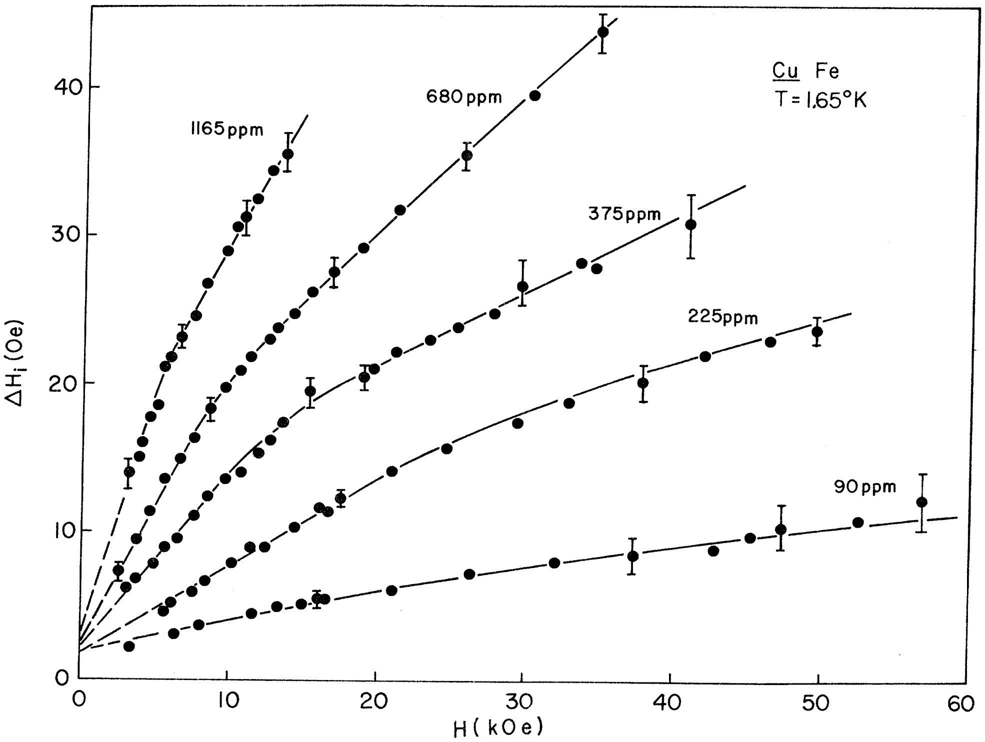

FIG. 2. Magnetic field dependence of the Fe-impurity contribution to the Cu^{63} NMR linewidth ΔH_i, at 1.65 °K for the same samples as in Fig. 1.

superparamagnetic clusters[4] and to magnetic Fe pairs.[6]

The Fe-impurity contribution to the Cu linewidth can be obtained following the method of Sugawara.[2] The total line shape $I(H)$ of the inhomogeneously broadened host NMR line in a dilute random alloy is given by

$$I(H) = \int_{-\infty}^{\infty} G(H - H')L(H')\,dH' \quad , \qquad (1)$$

where $G(H)$ is the Gaussian line shape of the host, and $L(H)$ is the intensity distribution function of the local fields at the host nuclei arising from the random distribution of impurities. Sugawara numerically extracted the impurity contribution to the Cu linewidth ΔH_i and showed that $L(H)$ is well approximated by a cutoff Lorentzian function. We have repeated these numerical calculations in order to obtain greater accuracy in the ΔH_i values than can be obtained from the plot in Sugawara's paper.[2]

In Figs. 2 and 3 we show the field dependence of ΔH_i at 1.65 °K. These data clearly show that the anomaly in the field dependence of ΔH_i first observed in *Cu*Fe (on a 410-ppm sample at 0.5 °K) by Heeger *et al.*[3] occurs over a wide concentration range.

The field-dependent part of ΔH_i for each sample shown in Figs. 2 and 3 can be divided into two distinct regions of different slope $S = d\Delta H_i/dH$. The data exhibit a constant slope S_L at low fields (but for $H > 2$ kOe) and also a constant slope S_H of smaller magnitude at higher fields. The data in Fig. 4 taken at 4.2 °K show that the change in the slope of ΔH_i vs H is still quite pronounced at this temperature. Golibersuch and Heeger[4] in their analysis of the *Cu*Fe data of Heeger *et al.*[3] (treating the *Cu*Fe data in terms of "quasiparticle" effects) associated the high-field slope S_H with simple RKKY line broadening. They referred to the larger magnitude of S_L as being due to the buildup of extra impurity-spin–conduction-electron-spin correlations. We shall carry over this terminology in referring to the low-field behavior as an enhancement of S_H. Consideration of the temperature dependence of these effects will show this approach to be more reasonable than the alternate one of considering the high-field behavior as a depression of S_L.

In Figs. 5(a) and 5(b) we plot the values of S_L and S_H at 1.65 and 4.2 °K, respectively, vs the Fe concentration as determined by atomic absorption analysis. A linear variation of both S_L and S_H with increasing Fe concentration is clearly evident in these curves. At both temperatures, S_L and S_H extrapolate to zero slope at $c = 0$. Fits to these curves give $S_L/c = (2.83 \pm 0.10) \times 10^{-6}$ and $S_H/c = (1.50 \pm 0.10) \times 10^{-6}$ (c in ppm) at 1.65 °K, while

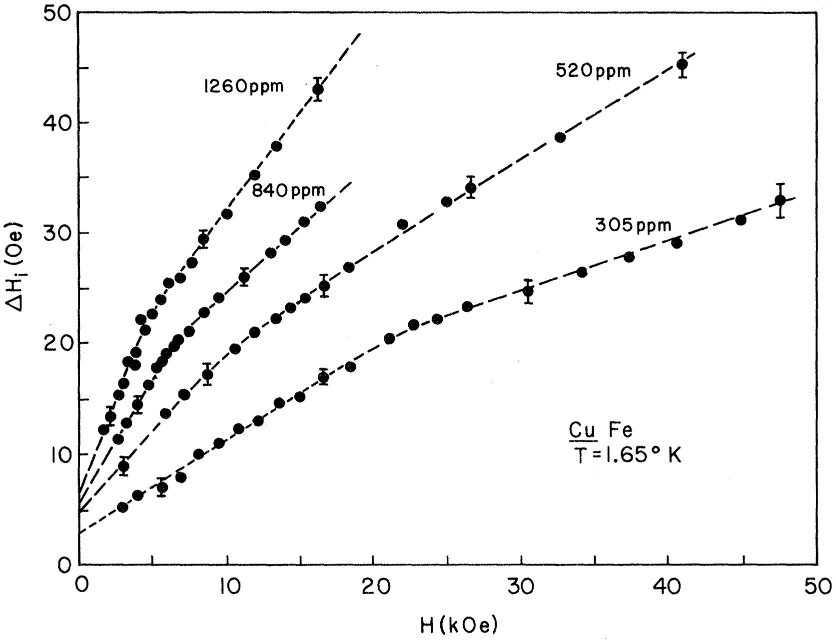

FIG. 3. Magnetic field dependence of the Fe-impurity contribution to the Cu^{63} NMR linewidth, ΔH_i, at 1.65 °K for *Cu*Fe samples containing 305-, 520-, 840-, and 1260-ppm Fe.

at 4.2 °K, S_L and S_H have decreased to $S_L/c = (2.21 \pm 0.15) \times 10^{-6}$ and $S_H/c = (1.33 \pm 0.15) \times 10^{-6}$. Figures 5(a) and 5(b) demonstrate that the field-dependent part of the impurity-induced linewidth is directly related to the behavior of single Fe impurities. Having established the linear dependence of S_L on c, we normalize our concentrations to the fit of S_L vs c at 1.65 °K, where we were able to

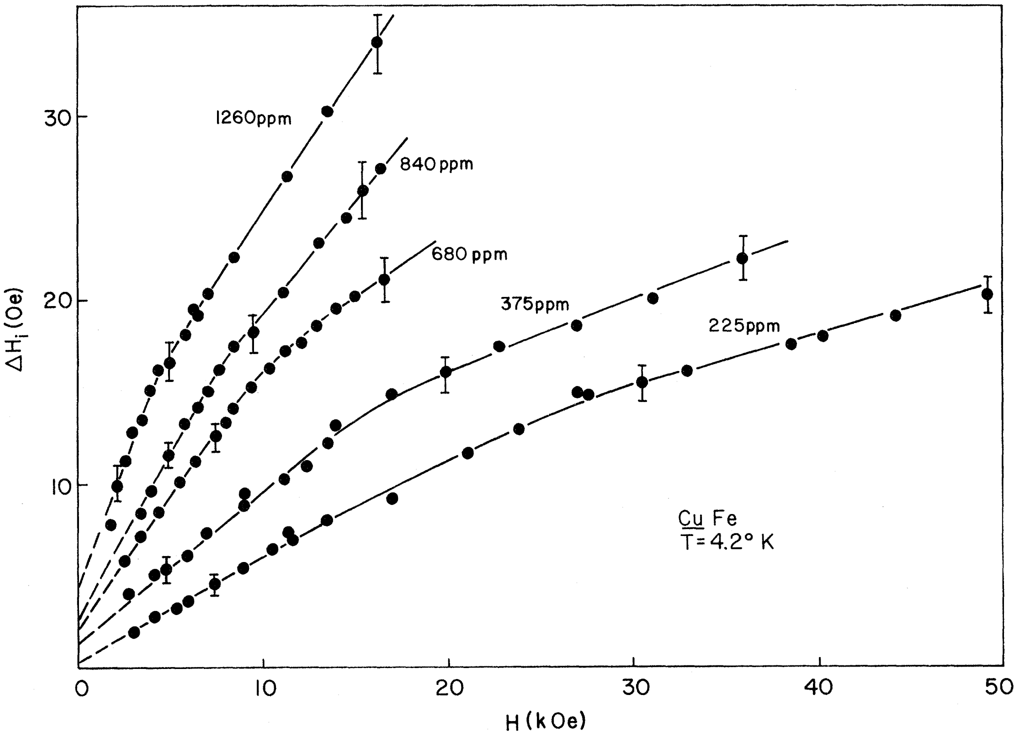

FIG. 4. Magnetic field dependence of the Fe-impurity contribution to the Cu^{63} NMR linewidth ΔH_i, in *Cu*Fe at 4.2 °K for samples containing 225-, 375-, 680-, 840-, and 1260-ppm Fe.

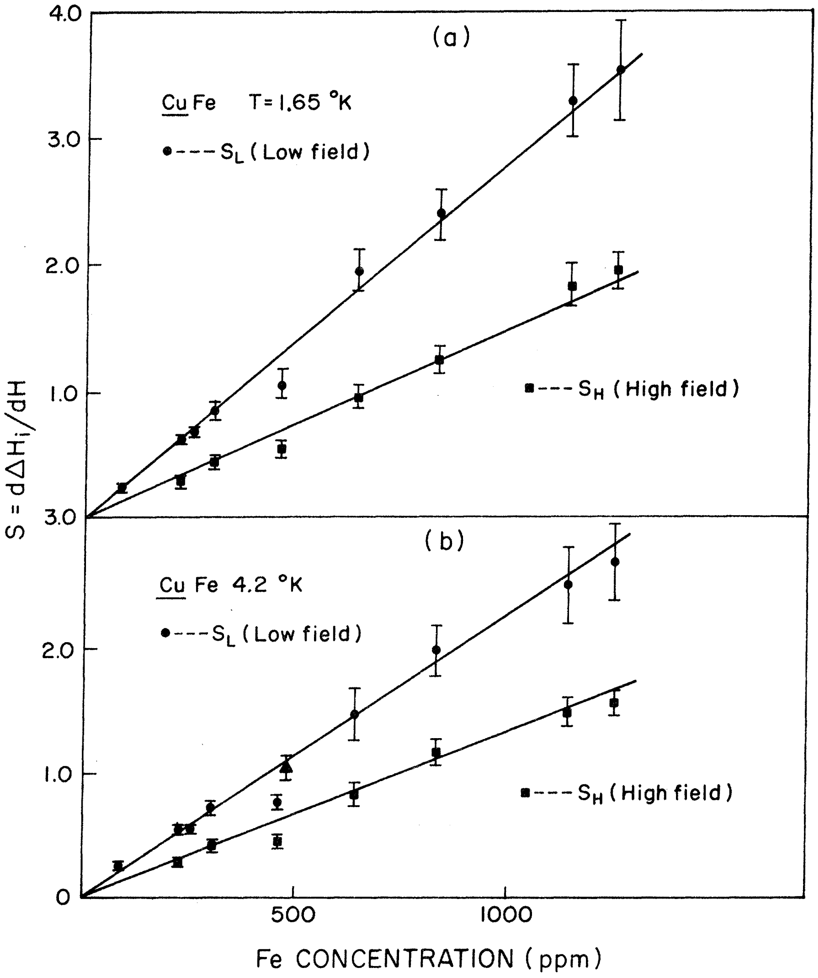

FIG. 5. Fe-concentration dependence of the low- and high-field slopes, S_L and $S_H (S = d\Delta H_i/dH)$, for the Cu^{63} NMR-linewidth data in *Cu*Fe at the temperatures (a) 1.65 °K and (b) 4.2 °K. The S_L point at 4.2 °K for the 480-ppm Fe is from Golibersuch and Heeger (Ref. 4).

obtain our most accurate data; i.e., we let $c = S_L \times 10^6/(2.83 \pm 0.10)$ (ppm). These values are used to label the curves in Figs. 1–4.

An additional affirmation of the fact that we are observing a single-impurity behavior may be seen in Figs. 6(a) and 6(b), where the ratio S_L/S_H is plotted vs c for $T = 1.65$ and 4.2 °K, respectively. The mean values of S_L/S_H are $S_L/S_H = 1.91$ at 1.65 °K and $S_L/S_H = 1.75$ at 4.2 °K. Clearly, this ratio is independent of *c irrespective of any determination of c*. Thus from the linear concentration dependence of S_L and S_H as shown in Figs. 5(a) and 5(b), as well as the concentration independence of the ratio S_L/S_H shown in Figs. 6(a) and 6(b), we conclude that the enhancement of the Fe-impurity contribution to the inhomogeneous broadening of the Cu NMR line results from the behavior of single Fe impurities and does *not* result from Fe-pair or large-Fe-cluster effects as has been suggested by several authors.[6,9]

No evidence is found for a c^2-dependent contribution to the field-dependent NMR linewidth as might be expected from the bulk magnetization data of Tholence and Tourner.[6] They show the c^2 contribution to the bulk magnetization to be equal to the linear contribution at about 340 ppm. The fact that we observe no c^2 term in our linewidth measurements is probably a consequence of a larger effective magnetic wipeout number for Cu nuclei around (either nearly magnetic or magnetic) pairs of Fe atoms in comparison to the isolated impurity wipeout number. This seems reasonable as Cu nuclei "seeing" the much larger oscillatory spin polarization around an Fe pair will increase the absorption in the wings of the resonance line but not in the central part of the resonance line. Thus an Fe pair would not be expected to contribute to the central part of the resonance line (and hence ΔH) unless the Cu nuclei are far enough from the Fe pair that the magnitude of the oscillatory spin polarization is comparable to that around the isolated Fe impurities outside the wipeout radius. As a result the relatively small number of Fe pairs should have little effect on the linewidth measurements (although this argument does not necessarily hold for the more complicated dynamic effects which depend

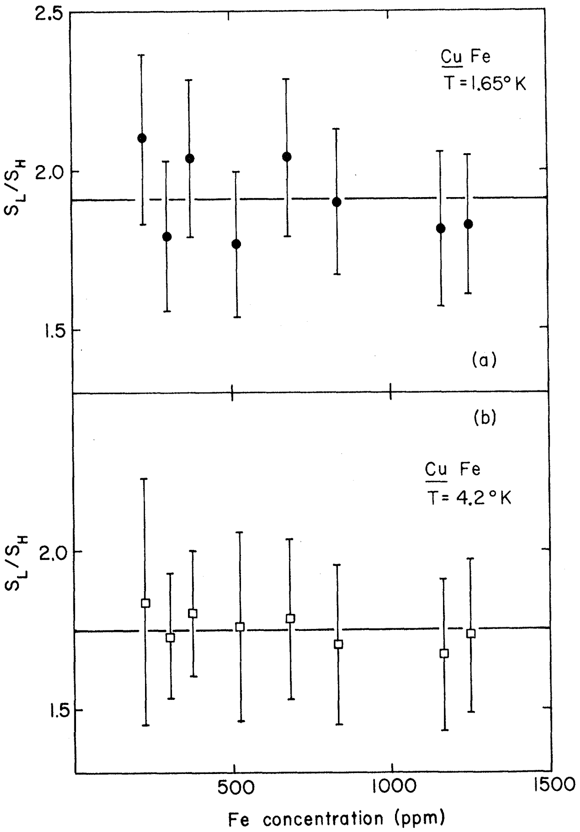

FIG. 6. Fe-concentration dependence of the ratio S_L/S_H of the low- and high-field slopes of the Cu^{63} NMR-linewidth data in *Cu*Fe for (a) 1.65 °K and (b) 4.2 °K.

upon the fluctuations of the impurity spins). We have estimated that the effective wipeout radius for an Fe pair having an effective "Kondo temperature" of 5 °K (suggested for the nearly magnetic pairs behavior by Tholence and Tournier[6]) is $r_c \approx 13$ Å as compared to the value of $r_c \approx 9$ Å obtained for a single Fe impurity by Golibersuch.[10]

An important aspect of the field dependence of ΔH_l is the concentration dependence of the applied field H_c defining the transition from S_L to S_H. Taking H_c as the field at which $S - S_H$ is one-half the value of $S_L - S_H$, we find that H_c depends inversely on the Fe concentration, as shown in Fig. 7(a). However, if we are indeed observing a single-impurity behavior in the low-field enhancement of S_H, the value of H_c must approach a concentration independent value $c \rightarrow 0$. As shown in Fig. 7(a), a deviation from the $1/c$ dependence of H_c may occur for the lowest-concentration (90 ppm) sample investigated. However, due to a slight magnetic field inhomogeneity in the superconducting magnet, a small correction must be made to the highest-field data for the 90-ppm sample leading to a somewhat larger uncertainty in these points as shown in Fig. 2 and a correspondingly increased uncertainty in the value of H_c. Thus, while a possible deviation from the $1/c$ dependence of H_c in Fig. 7(a) would seem to indicate that H_c $(c \rightarrow 0)$ is between 30 and 60 kOe, no conclusive statement can be made on this point.

In Fig. 7(b) the value of ΔH_l at H_c, designated ΔH_c, is plotted vs concentration. The value of ΔH_c is essentially concentration independent with a mean value of 20.2 ± 0.5 Oe at 1.65 °K. Similar results were obtained at 4.2 °K giving a mean value of ΔH_c at 4.2 °K of 15.0 ± 0.5 Oe.

The temperature dependences of these enhancement effects are shown in Fig. 8 for a 680-ppm sample. In Fig. 8, ΔH_l-vs-H plots are presented for a number of temperatures between 1.65 and 77 °K. Similar results were obtained for the other samples for which this temperature dependence was investigated. The enhancement of S_H described above is apparent in Fig. 8 for all temperatures below 18 °K for the 680-ppm sample. For $T \gtrsim 18$ °K the precision of the data does not permit the determination of two distinct slopes for these samples;

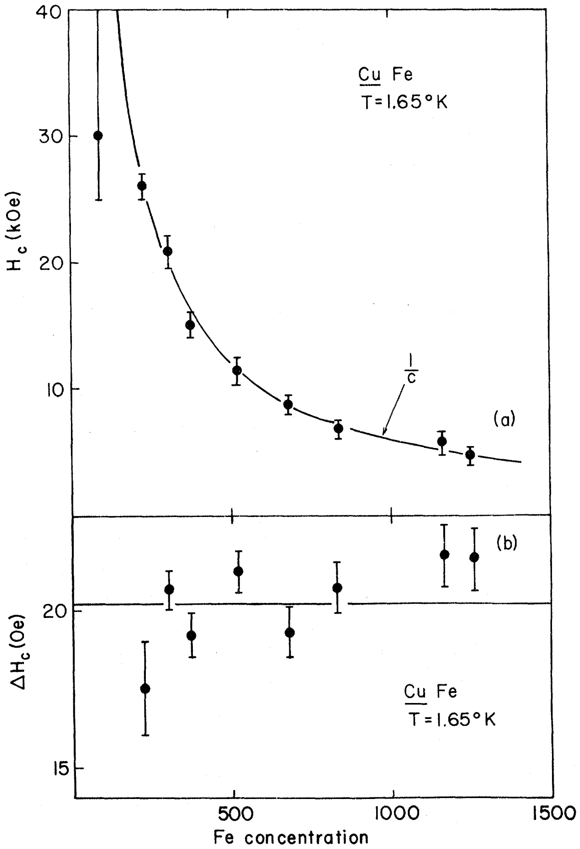

FIG. 7. (a) Concentration dependence of the field H_c defining the transition from S_L to S_H for the Cu^{63} NMR-linewidth data at 1.65 °K. (b) The concentration dependence of $\Delta H_c = \Delta H_l(H_c)$, the value of ΔH_l at the field H_c at 1.65 °K.

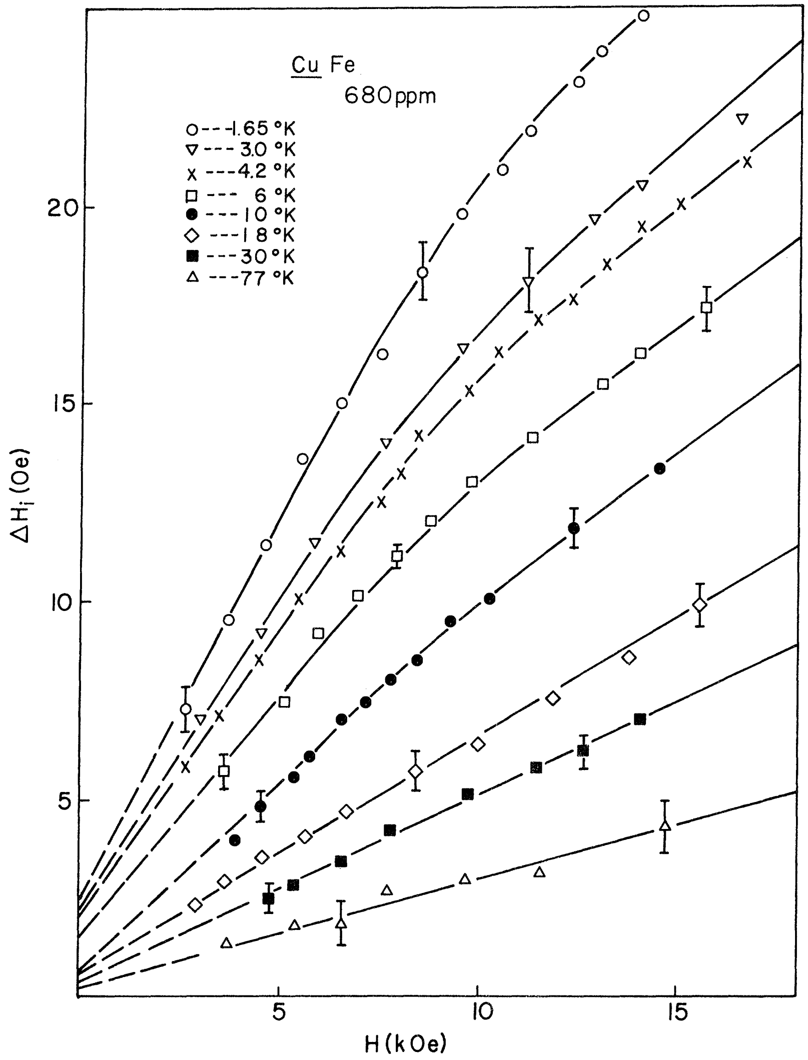

FIG. 8. Magnetic field dependence of the Fe-impurity contribution to the Cu^{63} NMR linewidth ΔH_i in *Cu*Fe for a 680-ppm sample for temperatures from 1.65 °K to 77 °K.

i.e., $S_L = S_H$ within our experimental uncertainty for $T \gtrsim 18$ °K.

A number of magnetization and susceptibility measurements have been made on dilute *Cu*Fe alloys in order to determine the single-impurity contribution. Unfortunately there is some disagreement as to the actual temperature dependence of the single-impurity susceptibility for magnetic fields above 2 kOe. Tholence and Tournier,[6] who have made magnetization measurements up to 60 kOe, concluded that the single-impurity behavior may be described by

$$\langle S_z\rangle = (1/g\mu_B)[\mu_{\rm eff}^2 H/3k(T+29)] \qquad (2)$$

down to 1 °K, where $\mu_{\rm eff} = 3.4\mu_B$. Other investigators[11] have stated that the temperature dependence at low temperatures is $\langle S_z\rangle \propto (T+16)^{-1}$. Since Tholence and Tournier have explicitly separated the Fe-pair contributions from the single-impurity contributions, we will take their result.

For the purpose of comparing our NMR measurements with bulk-susceptibility measurements,[6] which give $\chi \propto (T+\theta)^{-1}$, where $\theta = 4.5T_K \approx 29$ °K, we have plotted S_L vs $(T+29)^{-1}$ in Fig. 9. If the Cu NMR linewidth were broadened solely through interactions of the nuclei with the RKKY-type conduction-electron-spin polarization scaling with $\langle S_z\rangle$ we should then find that $S_L \propto \langle S_z\rangle/H \propto (T+29)^{-1}$ at all temperatures. While this is the behavior observed at high temperatures, S_L increases more rapidly than $\langle S_z\rangle/H$ as the temperature is decreased below $T \simeq 18$ °K. Golibersuch and Heeger[4] observed a similar behavior for a *Cu*Fe sample ($c = 480$ ppm) which is also shown in Fig. 9. In Fig. 10, S_H is plotted against $(T+29)^{-1}$ for three samples. In contrast to the behavior of S_L, S_H is reasonably well fit by a $[T+29(\pm 5)]^{-1}$ variation over the entire temperature range. For the 305-ppm sample the $T > 4.2$ °K measurements were not extended to the high fields necessary to observe the change in

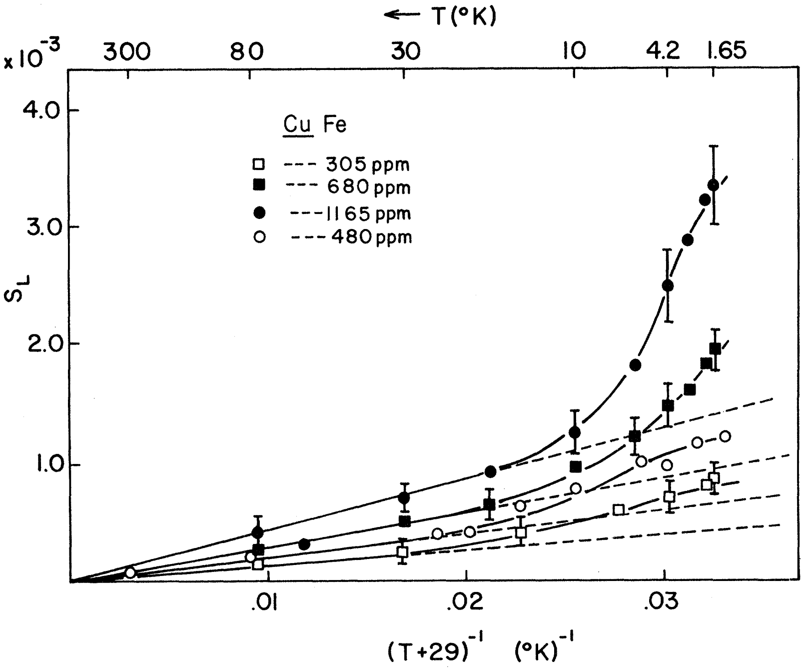

FIG. 9. Slope S_L ($S = d\Delta H_t/dH$) vs $(T+29)^{-1}$ for several *Cu*Fe samples of different Fe concentration. $(T+29)^{-1}$ is the temperature dependence of the single-impurity contribution to the bulk susceptibility as determined by Tholence and Tournier (Ref. 6). The data for the 480-ppm sample were taken from Golibersuch and Heeger (Ref. 4).

slope, so S_H could not be determined in the range 18 °K > T > 4.2 °K for this sample. For the temperature range of 18 °K < T < 77 °K, we have taken $S_H = S_L$. The ratio of S_L/S_H builds up rapidly with decreasing temperature below 18 °K, reaching a "half-amplitude" point at $T_c \approx 6$ °K independent of the Fe concentration. This value of T_c is almost identical to the value of the T_K determined from the susceptibility measurements. While the full amplitude of S_L/S_H occurs only at 0 °K, a plot of S_L vs T^{-1} shows that S_L attains a nearly temperature-independent value by 1.65 °K (we estimate this is within 10% of the 0 °K value). The variation of H_c with temperature was determined up to 10 °K. Over this limited temperature range H_c appears to be temperature independent. On the other hand, the values of ΔH_c shown in Fig. 11 decrease as $[T+5(\pm 2)]^{-1}$.

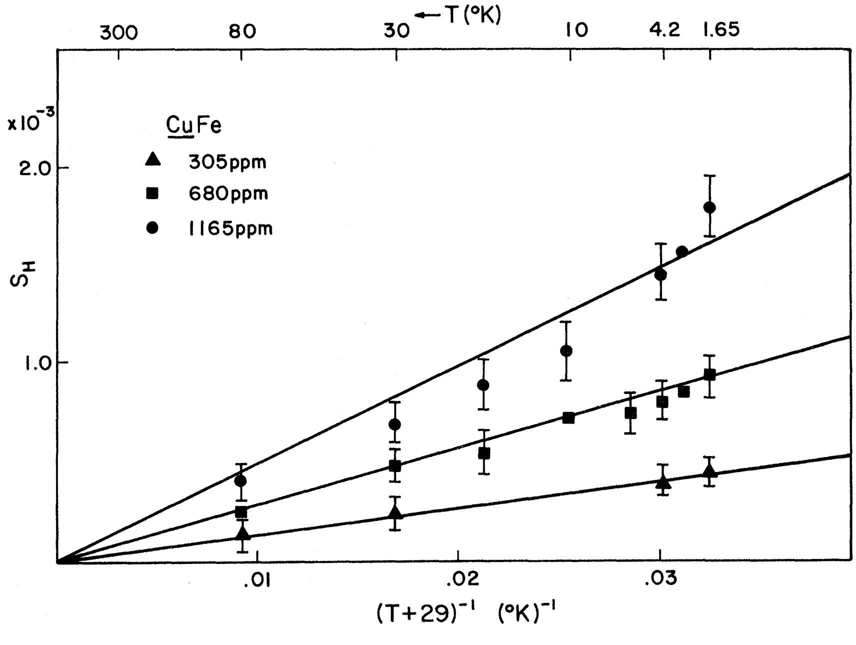

FIG. 10. Slope S_H ($S = d\Delta H_t/dH$) vs $(T+29)^{-1}$ for several *Cu*Fe samples of different Fe concentration.

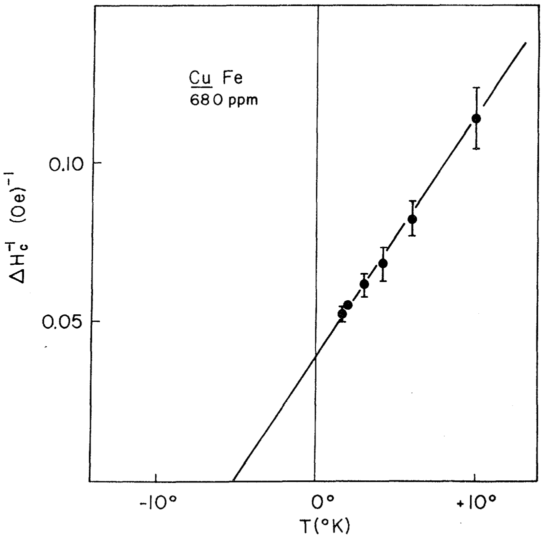

FIG. 11. Temperature dependence of $\Delta H_c \equiv \Delta H_i(H_c)$, the value of ΔH_i at the field H_c.

The data presented in this section indicate the following. At either high temperature ($T \gg T_c$) or high field ($H \gg H_c$), the Cu NMR linewidth is broadened through interactions of the Cu nuclei with the ordinary perturbative RKKY-type conduction-electron-spin polarization. As the temperature is lowered through T_c, the oscillatory spin polarization increases and is reflected in the temperature-dependent line broadening of the host NMR. We may extract the intrinsic temperature dependence of the extra oscillatory spin polarization from Fig. 9 by subtracting the $(T+29)^{-1}$ fit from the values of S_L. We shall define a quantity $\xi(H,T)$ such that

$$\xi(H,T) \equiv \frac{S(H,T) - S_H(T)}{S_L(0\ ^\circ\mathrm{K}) - S_H(0\ ^\circ\mathrm{K})} , \tag{3}$$

and take $S_L(1.65\ ^\circ\mathrm{K}) = S_L(0\ ^\circ\mathrm{K})$ and $S_H(1.65\ ^\circ\mathrm{K}) = S_H(0\ ^\circ\mathrm{K})$. In Fig. 12, $\xi(H,T)$ is plotted vs T/T_c in the field region $H \ll H_c$. This plot is analogous to the "quasiparticle amplitude" plot of Golibersuch and Heeger.[4] In Fig. 13, $\xi(H,T)$ is plotted against the reduced field H/H_c for several samples at 1.65 °K. The data of Fig. 13 clearly show that the field dependence of $\xi(H,T)$ can be characterized by the field parameter H_c. Comparing the field and temperature dependence of $\xi(H,T)$ it is clear that $\xi(H,T)$ falls to zero rather sharply as the field is increased through H_c, while the decrease of $\xi(H,T)$ with increasing temperature is more gradual. This effect may be even more dramatic than shown in Fig. 13. Since the value of H_c depends strongly on the Fe concentration, while T_c does not, the transition region for $\xi(H,T)$ shown in Figs. 12 and 13 may be broadened in field but not in temperature as a result of spatial fluctuations of the local Fe concentration.

B. Cu^{63} Spin-Lattice Relaxation Time T_l

The Cu^{63} spin-lattice relaxation time T_l was measured in the *Cu*Fe alloys on which the linewidth measurements were made. The enhancement of the Cu relaxation rate above the pure-Cu value was determined from 1.4 to 4.2 °K in applied fields

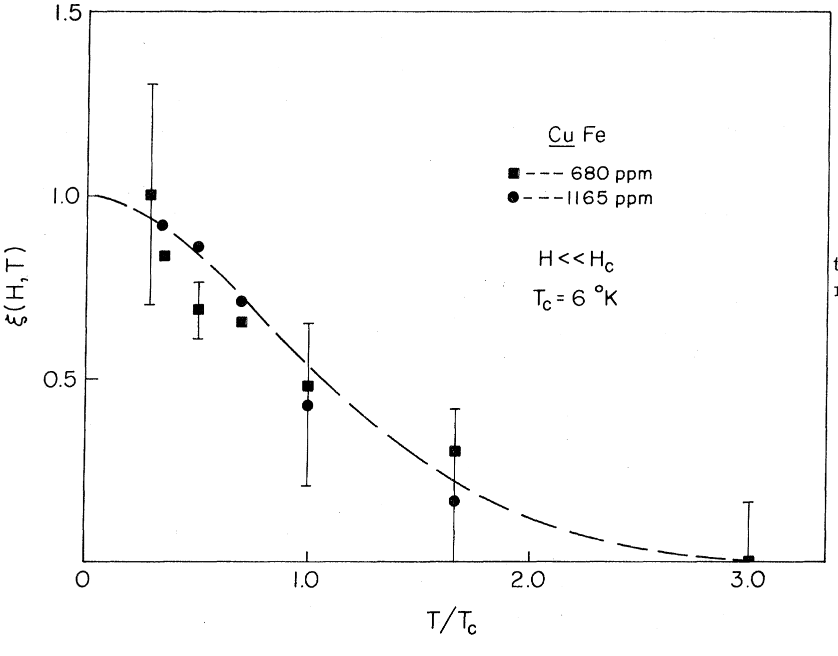

FIG. 12. Temperature dependence of the function $\xi(H,T)$ for $H \ll H_c$ using the reduced temperature T/T_c.

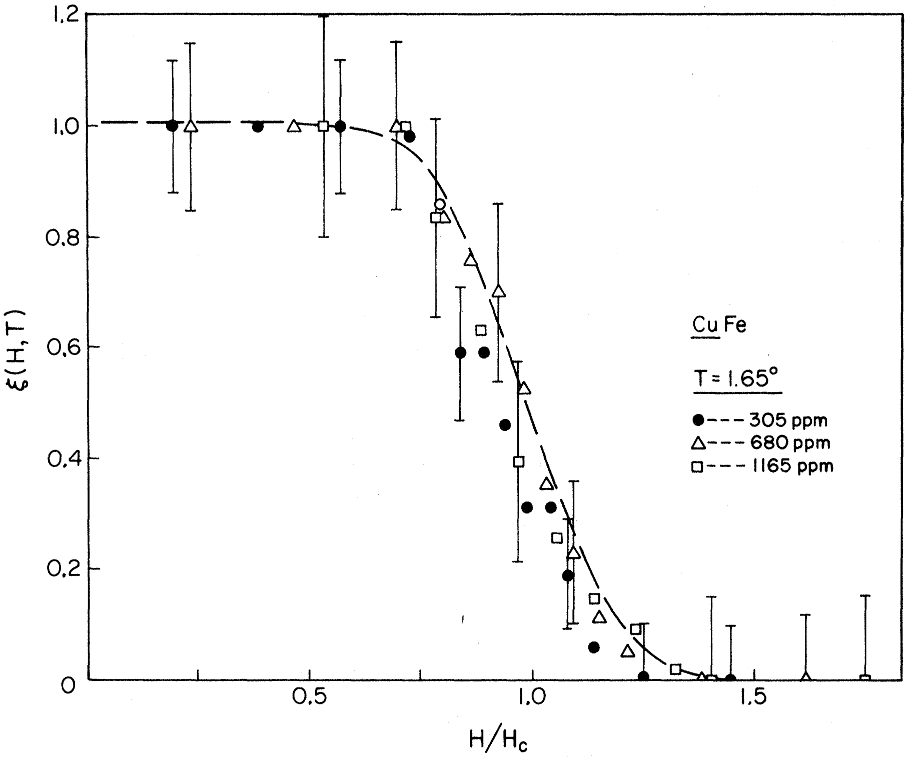

FIG. 13. Magnetic field dependence of the function $\xi(H, T)$, plotted using H/H_c, for 1.65 °K.

of 2.5 to 16 kOe, for Fe concentrations from 0 to 1260 ppm. The relaxation rate at 77 °K and 7.5 kOe was also measured. The relaxation time was obtained by monitoring the recovery of the spin-echo amplitude at a time t after the application of a comb of rf pulses which saturated the Cu NMR, except for the 77 °K data where a 180°-90° sequence was employed. Single exponential decay was observed over almost two decades in $[M_z(\infty) - M_z(t)]$ for almost all cases, although for some of the most concentrated samples ($c > 1000$ ppm) we observed a slight nonexponential behavior in the recovery at very small t (t within 50 msec of the saturating comb) at liquid-helium temperatures. This small deviation from nonexponential behavior can be quantitatively accounted for by incomplete saturation of the $|\frac{3}{2}| \leftrightarrow |\frac{1}{2}|$ transitions.[12] Values of T_1 reported in this work were determined only from the long exponential (at least one decade) tail of the $[M_z(\infty) - M_z(t)]$ decay curves and thus we avoided any problems resulting from incomplete saturation of the Cu^{63} $|\frac{3}{2}| \leftrightarrow |\frac{1}{2}|$ transitions.

The impurity-induced relaxation rate, T_{1i}^{-1} is given by $T_{1i}^{-1} = T_1^{-1}$ (measured) $- T_{1K}^{-1}$ (Cu), where T_{1K}^{-1} (Cu) is the Korringa relaxation rate of the pure-Cu host. We measured a value of T_{1K} (Cu)$T = 1.23 \pm 0.03$ sec °K for pure Cu from 1.4 to 4.2 °K using the same experimental conditions and saturating comb under which the alloys were measured. Such a procedure minimizes any systematic error which might arise in determining T_{1i}^{-1}. Our pure-Cu value is in good agreement with previously determined values of 1.23 to 1.28 sec °K given in the literature.[13–15] We estimate the uncertainty in our measurements of the experimental relaxation rates to vary from 2.5% in pure Cu to about 6% in the most concentrated samples.

In a preliminary report[7] on the enhancement of the Cu relaxation rate in *Cu*Fe alloys we presented data on T_1 vs Fe concentration. In agreement with Hanabusa and Kushida[14] (hereafter referred to as HK) we concluded that in the temperature range investigated, the excess relaxation rate is linear in Fe concentration for $c \lesssim 300$ ppm for $2.5 < H < 15$ kOe. However, the linear region appears to extend to higher concentrations at higher magnetic fields. At 15 kOe, for example, the excess rate is best fit by a linear Fe-concentration dependence up to 1260 ppm. Above 400 ppm and for lower magnetic fields, the excess rate increases more rapidly with increasing Fe concentration but appears to become linear again at the higher Fe concentrations. Linear extrapolation of the lowest-concentration data to zero concentration gives the pure-Cu rate as expected. Since it is the single-impurity contribution in which we are interested, and in order to be able to compare our data with existing theories, we will confine our attention primarily to the region ($0 < c \lesssim 400$ ppm). Figure 14 displays the low-concentration data on an expanded scale and

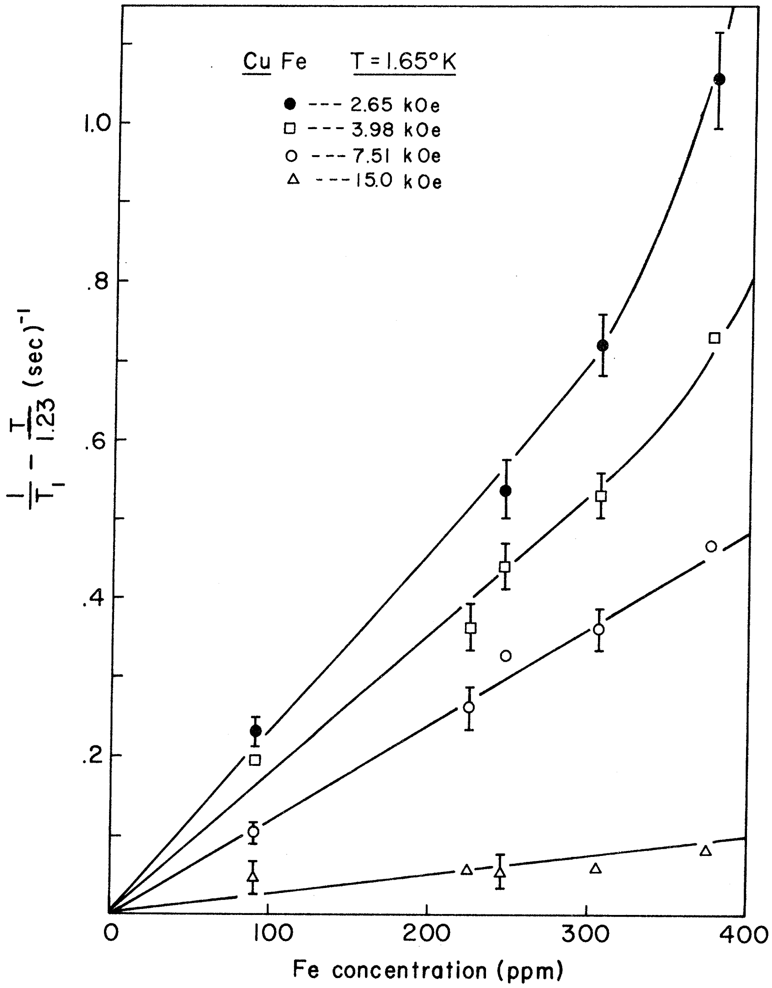

FIG. 14. Concentration dependence ($0 < c < 400$ ppm) of the impurity-induced excess Cu^{63} NMR spin-lattice relaxation rate in *Cu*Fe at 1.65 °K for magnetic fields from 2.65 to 15 kOe.

shows that the data are well represented by $T_{1i}^{-1} \propto c$ in the low-concentration region.

The magnetic field dependence of T_{1i}^{-1} is plotted in Fig. 15 for three of the low-concentration samples at 1.65 °K. Also included on this plot are data points of HK at 4 and 8 MHz.[14] Their data are in reasonable agreement with ours, within the limits of uncertainty of the experiments. We observe that there is quite a substantial field dependence in this region, and that the enhancement above the host relaxation rate has almost completely disappeared at an applied field of 16 kOe.

The temperature dependence of the excess relaxation rate is plotted in Figs. 16(a) and 16(b) for two low-Fe-concentration samples. In Fig. 16(a) the temperature dependence of the excess rate, $(T_{1i}T)^{-1}$, is displayed for a 305-ppm sample. These data are typical for the dilute alloys. We have plotted $(T_{1i}T)^{-1}$ rather than T_{1i}^{-1} to conveniently show the very low-temperature data of Welsh *et al.*,[16] who found $(T_{1i}T)^{-1}$ to be independent of temperature ($0.03\ ^\circ\mathrm{K} < T < 0.3\ ^\circ\mathrm{K}$) and independent of or only weakly dependent on field.

The excess relaxation-rate data for the more dilute *Cu*Fe alloys are summarized in Fig. 17, where $T(cT_{1i})^{-1}$ is plotted vs T/H. Included in Fig. 17 are data from HK.[14] The scatter in the data when comparing different samples results from the uncertainty in the Fe concentration, while the error bars represent the uncertainty in the measurements.

Careful measurements of T_1^{-1} at 77 °K and 7.5 kOe on the 305- and 1165-ppm samples were made in order to determine whether any enhancement of T_1^{-1} exists at this temperature. The relaxation rate was measured in each case under identical conditions and with the samples immersed in liquid nitrogen. These results are summarized in Table I. The enhancement at 77 °K, if any exists, is quite small. These measurements, however, allow us to place an upper bound on the enhanced rate for this temperature of $0 \leq T_{1i}^{-1} < 2.3 \times 10^{-3} c$ (sec^{-1}) where c is given in ppm.

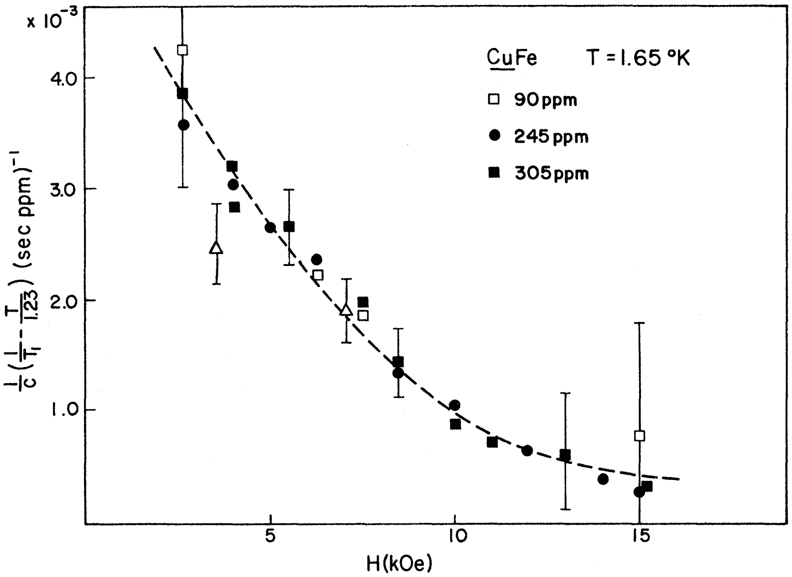

FIG. 15. Magnetic field dependence of the impurity-induced excess Cu^{63} NMR spin-lattice relaxation rate in *Cu*Fe at 1.65 °K. The points denoted by the triangles are taken from Hanabusa and Kushida (Ref. 14).

IV. DISCUSSION

A. Host NMR Linewidth

The data presented in Sec. III show that in the Kondo system *Cu*Fe the single-impurity contribution to the host linewidth exhibits an anomalous behavior for $T < T_K$ which may be summarized as follows.

(i) At liquid-helium temperatures we find two distinct regions of constant slope for $H > 2$ kOe. The transition from the slope at low fields, S_L, to the smaller magnitude slope at high fields, S_H, occurs in a relatively narrow range of applied fields centered at H_c.

(ii) This behavior results from the *single-impurity* contribution as evidenced by the linear concentration dependence of both S_L and S_H and particularly by the concentration independence of the ratio of S_L/S_H.

(iii) From 1.65 to 77 °K, S_H is consistent with the $(T+29)^{-1}$ temperature dependence observed for the single-impurity contribution to the bulk susceptibility. However, S_L varies as $(T+29)^{-1}$ for $T \gtrsim T_K$ but is enhanced for $T \lesssim 18$ °K. The magnitude of this enhancement varies from $S_L/S_H = 1.9$ at 1.65 °K to $S_L/S_H = 1$ at 18 °K with a half-amplitude point $T_c \approx 6$ °K which is concentration independent.

(iv) The applied field H_c is nearly temperature independent and varies as c^{-1} except perhaps as $c \to 0$. The linewidth ΔH_c is concentration independent and decreases to half its 1.65 °K value at about 8 °K.

(v) The field and temperature dependence of the enhancement of the single-impurity contribution to the host NMR linewidth is characterized by the function $\xi(H, T)$ shown in Figs. 12 and 13.

In this section we show that these points may be consistently accounted for in terms of the enhancement of the oscillatory conduction-electron-spin

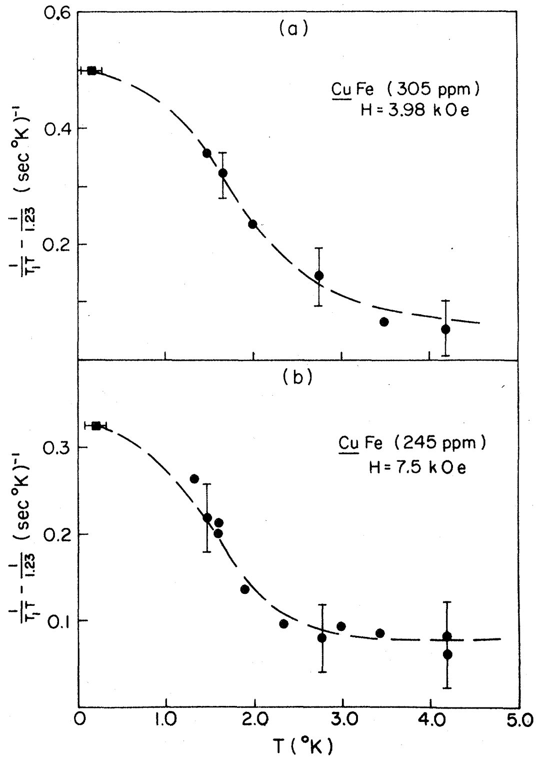

FIG. 16. Temperature dependence of the impurity-induced excess Cu^{63} NMR spin-lattice relaxation rate in *Cu*Fe for (a) a 305-ppm sample at 3.98 kOe; (b) a 245-ppm sample at 7.5 kOe. The very low-temperature points are taken from Welsh *et al.* (Ref. 16).

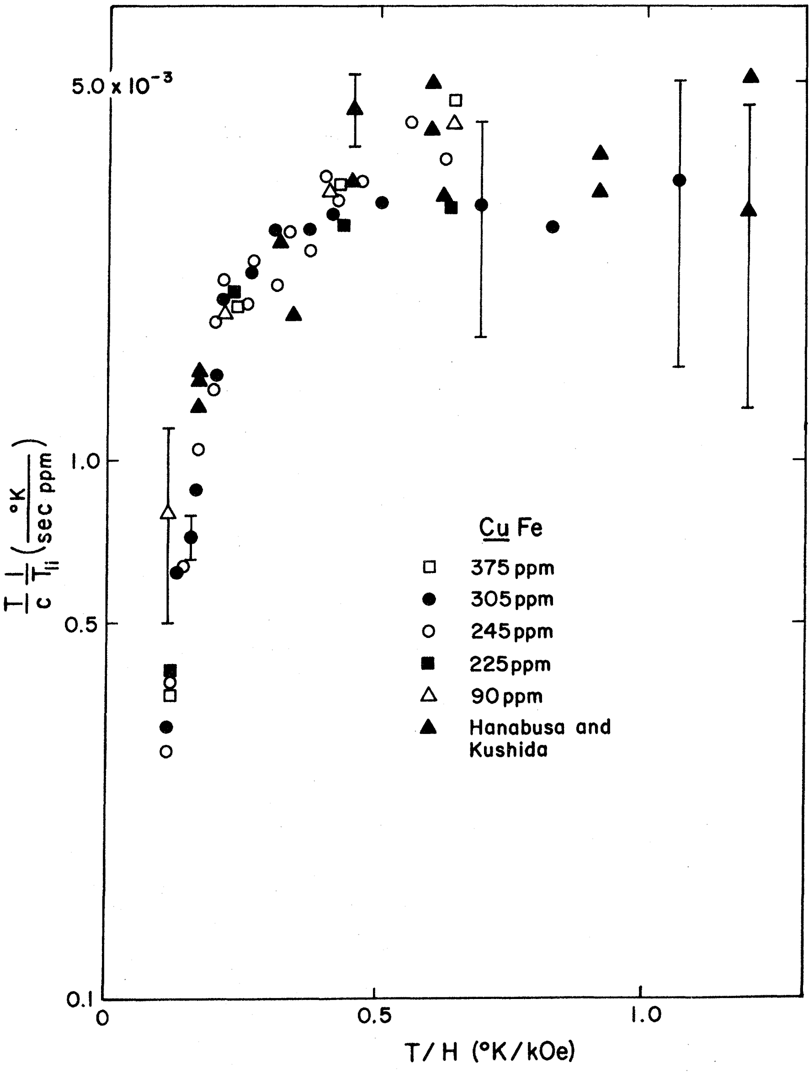

FIG. 17. Impurity-induced excess Cu^{63} NMR spin-lattice relaxation rate in *Cu*Fe plotted as $T(c\,T_{1i})^{-1}$ vs T/H for 90-, 225-, 305-, and 375-ppm Fe. The solid triangles are taken from Hanabusa and Kushida (Ref. 14).

polarization around an Fe impurity in the Kondo state.

The quantity H_c characterizes the field at which the extra oscillatory spin polarization attains saturation. Golibersuch and Heeger[4] interpreted H_c as indicating the magnetic energy necessary to destroy the "quasiparticle-spin-polarization cloud" formed from the conduction-electron spins near the impurity. While the existence of the "quasiparticle" has been questioned, in part as a result of the magnetization measurements of Tholence and Tournier,[6] it is clear from the data presented in Sec. III that additional correlations exist between the impurity spin and the conduction-electron spins other than the simple perturbative RKKY-type spin polarization present for $T \gg T_K$. The fact that H_c varies inversely with the Fe concentration suggests the existence of interactions between Fe spins of sufficient magnitude to effectively saturate the extra low-temperature oscillatory conduction-electron-spin polarization in successively smaller applied magnetic fields as the Fe concentration increases. However, at a given temperature, ΔH_c is independent of concentration, indicating that the effective field at the field H_c, $H_{\text{eff}}(H_c)$ is constant. This effective field must have an oscillatory spatial dependence[4] since only a small Knight shift is observed.[2] Treating these interactions in the molec-

TABLE I. Cu^{63} spin-lattice relaxation time at 77 °K and 7.5 kOe in *Cu*Fe.

Fe concentration (ppm)	T_1 (msec)	T_1T (sec °K)	$(c\,T_{1i}T)^{-1}$ 10^5(sec °K ppm)$^{-1}$
0	16.46 ± 0.24	1.268 ± 0.019	0.000
305	16.24 ± 0.35	1.25 ± 0.027	3.6 ± 6.9
1165	16.13 ± 0.30	1.241 ± 0.023	1.4 ± 1.6
320[a]	16.01 ± 0.25	1.233 ± 0.020	5.5 ± 4.1

[a] Reference 14.

ular field approximation, we assume a time-averaged fluctuating field of the form

$$H_{\text{eff}}(H, T) = \eta(H, T)cH \quad , \tag{4}$$

where $\eta(H, T)$ is independent of concentration. Clearly H_c will be proportional to $1/c$, and $\Delta H_c \propto H_{\text{eff}}(H_c)$ will be independent of c.

The field and temperature dependence of $\eta(H, T)$ and hence the magnitude of the oscillatory spin polarization can be written in an explicit form using the function $\xi(H, T)$ from Eq. (3). The function $\xi(H, T)$ defines the region of the H-T plane within which the perturbative treatment of the oscillatory spin polarization breaks down. By the definition of $\xi(H, T)$ the single-impurity contribution to the host linewidth is

$$\Delta H_i(H, T) = S_H H[1 + (0.9/H) \int_0^H \xi(H', T)dH'] \quad , \tag{5}$$

where the constant 0.9 results from the value of S_L/S_H at 1.65 °K. From the observation that S_H results from the simple perturbative RKKY-type spin polarization about an impurity, so that $S_H \propto c\langle S_z \rangle/H$, Eq. (5) can be written as

$$\Delta H_i(H, T) \propto c\langle S_z \rangle \, [1 + (0.9/H) \int_0^H \xi(H', T)dH'] \quad . \tag{6}$$

Then, noting that $\Delta H_i(H, T) \propto H_{\text{eff}}(H, T)$, one obtains from Eq. (4) the result

$$\eta(H, T)H \propto \langle S_z \rangle \, [1 + (0.9/H) \int_0^H \xi(H', T)dH'] \quad , \tag{7}$$

which provides a phenomenological description of the field and temperature dependence of the magnitude of the long-range oscillatory spin polarization around an Fe impurity in Cu.

It is interesting to compare the thermal energy kT_c, needed to destroy the extra impurity-spin-conduction-electron-spin correlations with the magnetic energy $\mu_B H_c$ needed to saturate this extra oscillatory spin polarization. The thermal energy corresponds to $kT_c/\mu_B = 90$ kOe, while $H_c(c \to 0)$ was estimated to be between 30 and 60 kOe in Sec. III. Thus the difference between these two energies may not be as large as originally proposed.[4] In fact, given the uncertainties in both T_c and H_c, the thermal and magnetic energies could be the same. However, there is no *a priori* reason why H_c and kT_c/μ_B should be identical as pointed out by Golibersuch and Heeger.[4]

The strongest interaction between dilute magnetic impurities which might account for the magnitude of H_{eff} arises via the d-d double resonance mechanism originally proposed by Caroli.[17] The effective exchange constant for the d-d mechanism is $J = 20\, E_F \,|\sin\delta\,|/(3\pi S)$[18] (taking $\mathcal{H} = J\vec{\text{s}} \cdot \vec{\text{S}}$). For d resonance scattering, the difference δ of the spin-up and spin-down phase shifts is $\delta = (\pi/5)m$. Magnetization measurements yield an effective moment of $3.4\mu_B$ for *Cu*Fe,[6] indicating a saturation moment of $m = 3\mu_B$. These values result in an effective constant of $J \approx 8$ eV while s-d exchange constants are typically less than 1 eV. Thus, it is expected that the d resonance scattering mechanism should dominate the host NMR line broadening. The large value of $J(\simeq 5$ eV) found by Golibersuch and Heeger[4] to account for the host line broadening in *Cu*Fe is consistent with this value.

Narath and Gossard[19] have shown that the d-d mechanism satisfactorily accounts for the observed V and Ag linewidths in the *Au*V and *Au*(*Ag*)V systems. They calculate the host linewidth between the half-amplitude points $\Delta H_{1/2}$ from the d resonance mechanism to be

$$\frac{\Delta H_{1/2}}{H} = 15\chi_d \frac{|H_{\text{hf}}^{(s)} \sin\delta\,|}{2Nm\mu_B} \left\langle \left| \sum_j \frac{\cos(2k_F R_{ij})}{(k_F R_{ij})^3} \right| \right\rangle \quad , \tag{8}$$

where χ_d is the impurity susceptibility, $H_{\text{hf}}^{(s)}$ is the host s-contact hyperfine field, and N is Avogadro's number. The average of the RKKY term in the brackets was computed to be $0.08c$ for *Au*V.[19] For *Cu*Fe, this gives a value $0.10c$, assuming a free-electron behavior and taking a ratio of atomic volumes of Cu to Au of 0.70. The impurity susceptibility may be obtained from the (high-field) data of Tholence and Tournier[6] to be $\chi_d = 5.1 \times 10^{-2}$ emu/g atom Fe. For $H_{\text{hf}}^{(s)}$ we take the neutral free-atom s-valence electron value of 2.6×10^6 Oe/μ_B reduced by a factor of 0.44 for Cu atoms in Cu metal.[20] Using these values in Eq. (8) we find $\Delta H_{1/2}/H = 2.6 \times 10^{-6}c$ (c in ppm) as compared with the experimental value of $2.1 \times 10^{-6}c$ for this quantity at 1.65 °K and at high fields ($H > H_c$). Thus the d resonance scattering mechanism does account quite well for the host linewidth in *Cu*Fe as well as in *Au*V.

This d-d mechanism causes large fluctuating fields at an Fe atom due to the sum of its couplings with all other Fe spins via the long-range oscillatory spin polarizations. At an Fe site there will be an average fluctuating field whose magnitude is given by[19]

$$H_{\text{eff}} = \frac{25E_F}{2\pi} \frac{\chi_d H}{N(m\mu_B)^2} \sin^2\delta \left\langle \left| \sum_j \frac{\cos(2k_F R_{ij})}{(k_F R_{ij})^3} \right| \right\rangle \tag{9}$$

Taking an effective d-spin susceptibility of $(S_L/S_H)\chi_d$ at low fields, we find that $H_{\text{eff}} \simeq \pm 0.8H$ for a 100-ppm sample. Thus, the average value of these fluctuating fields at an Fe site due to the d-d resonant couplings is comparable in magnitude to the applied field. From the fact that the distribution of effective fields is described by the function $L(H)$ from Eq. (1), fluctuations of H_{eff} at an Fe site can be an order of magnitude larger than that estimated from Eq. (9). Whether the *d-d* double-resonance mechanism actually accounts for the saturation of the extra oscillatory spin polarizations can only be determined by a complete treatment of the Kondo problem including these effective fields.

Unfortunately, most of the published theories treat the spin-spin correlation function $p(r) = \langle \vec{S} \cdot \vec{\sigma}(r) \rangle$ rather than the impurity-induced conduction-electron-spin polarization $\langle \sigma_z(r) \rangle = \langle (\vec{S} + \vec{\sigma}) \cdot \vec{\sigma}(r) \rangle$, so there are few theoretical results against which we can compare our NMR results. The correlation functions $p(r)$ resulting from several theoretical formulations have shown long-ranged negative-definite components in their spatial dependence.[1] If this spatial variation $[\sin^2 k_F r/(k_F r)^2]$ should also hold for the polarization, as found to be the case by Heeger *et al.*[3] for the Appelbaum-Kondo[21] polarization function, then this disturbance would cause a large Knight shift of the host metal. As pointed out by several authors,[4,19] the absence of this large Knight shift in *Cu*Fe[2] and *Au*V[19] indicates that there is no such spatially extended term in the conduction-electron-spin polarization.

Bloomfield *et al.*[22] predict that $(\langle S_z \rangle + \langle \sigma_z \rangle)$ will deviate from a Curie-Weiss law at low temperatures in a manner qualitatively similar to that observed in our linewidth measurements (Fig. 9). Comparison of this conclusion with experiment is hampered by apparently contradictory results for the temperature dependence of the susceptibility. The detailed measurements by Tholence and Tournier,[6] however, show no enhancement of the net impurity moment indicating that the net spin $(\langle S_z \rangle + \langle \sigma_z \rangle)$ varies as $H/(T+29)$ down to 1 °K. This implies that there is an enhancement of the oscillatory spin polarization around an impurity in the Kondo state due to the many-body spin correlations between the impurity and the conduction-electron spins which results in an enhanced host NMR linewidth, but in no net spin polarization.

Bloomfield *et al.*[22] also explicitly calculate the conduction-electron polarization. Their results show a polarization at low temperatures which is an order of magnitude smaller than, and opposite in sign to, $\langle S_z \rangle$. This polarization is oscillatory but contains a negative-definite component which is exponentially damped within a very short range, so its contribution would not be detectable in NMR experiments in agreement with experimental results on *Cu*Fe[2] and *Au*V.[19] (Those nuclei close enough to the impurity to sense any such short-range polarization would not contribute to the observed signal because of wipeout effects.) However, they obtain no long-range oscillatory spin polarization of sufficient magnitude to account for the enhancement of the host NMR linewidth reported here.

In the absence of further theoretical treatments of this question, little more can be said about the nature and form of the conduction-electron polarization. The present study has determined the intrinsic field and temperature dependence of this oscillatory spin polarization as it is reflected in the host NMR linewidth. We have also shown, in a consistent manner, that large fluctuating fields exist in *Cu*Fe because of the indirect coupling between the Fe spins via the *d-d* double-resonance mechanism.

Finally, we might speculate as to why these additional spin-correlation effects have been observed only in *Cu*Cr and *Cu*Fe and not in other Kondo systems such as *Cu*Mn ($T_K \simeq 0.05$ °K),[3] *Mo*Co ($T_K \simeq 24$ °K),[23] and *Au*V ($T_K \simeq 300$ °K).[19] Several factors must be considered. The first is that H_c seems to scale with the Kondo temperature [$H_c = 2.5$ kOe for a 46-ppm *Cu*Cr sample ($T_K \simeq 0.2$ °K)[3] while we have shown that H_c may be 30–60 kOe for a *Cu*Fe sample of this concentration]. Accordingly, H_c for *Cu*Mn would be expected to be 100 Oe or less. This very low-field range has not been studied in the *Cu*Mn NMR experiments. Secondly, the magnitude of the enhancement appears to increase as T_K decreases. The ratio of S_L/S_H for *Cu*Fe is 1.91 at 1.65 °K while in *Cu*Cr it is ≈ 4 for temperatures between 0.1 and 0.3 °K.[3] Thus, these effects may be too small to be observed in *Au*V. Also, the inverse-concentration dependence of H_c indicates that the magnetic fields and Co concentrations (0.1 to 1.0%) for the experiments on *Mo*Co were high enough that Co-Co couplings probably masked any enhancement of the spin correlations.[23]

B. Host Spin-Lattice Relaxation Rates

At present the enhancement of the host relaxation rate by magnetic impurities in the Kondo state is not well understood. Even for the region $T \gg T_K$ for which several calculations have been published, a number of questions remain unanswered. The most complete calculations for the enhancement of the host relaxation rate in the region $T \gg T_K$, have recently been published by Giovanninni *et al.*[24] They present a unified treatment of the relaxation process by real (BGS)[25] and virtual (GH)[26] excitations of the impurity spin via the RKKY interaction as well as the relaxation processes via the transverse (TD) and longitudinal (LD) fluctuations of the impurity magnetic dipole moment. Because of the difficulty in obtaining a valid order of magnitude estimate of the relaxation rate from each of these mechanisms, attempts to identify the dominant relaxation mechanism generally involve comparisons of the field and temperature dependence of the impurity-induced relaxation rate with the predictions of the GH, BGS, TD, and LD mechanisms. Unfortunately, due to insufficient data on the non-

Kondo alloy systems, a reliable identification has been made in very few systems.

The question of interest here is whether any of these high-temperature theories are valid in the $T < T_K$ region or whether they may be extended into the $T < T_K$ region by taking into account the susceptibility of an impurity in the Kondo state and the additional oscillatory conduction-electron-spin polarization at low temperatures. The functional forms of the relaxation mechanisms listed above are given by[24]

$$\left(\frac{1}{T_1}\right)_{\mathrm{GH}} \propto \frac{\langle S_z\rangle}{r_c^2}\frac{T}{H} \propto \frac{1}{r_c^2}\frac{B_S(X)}{X} \quad , \tag{10}$$

$$\left(\frac{1}{T_1}\right)_{\mathrm{BGS,TD}} \propto \frac{\langle S_z\rangle}{r_c^3}\frac{T}{H}\frac{\tau_2(\omega_n)}{1+(\omega_m\tau_2)^2}$$

$$\propto \frac{B_S(X)}{X}\frac{1}{r_c^3}\frac{\tau_2(\omega_n)}{1+(\omega_m\tau_2)^2} \quad , \tag{11}$$

$$\left(\frac{1}{T_1}\right)_{\mathrm{LD}} \propto \frac{1}{r_c^3}\left(\langle S_Z^2\rangle - \langle S_Z\rangle^2\right)\frac{\tau_1(\omega_n)}{1+(\omega_n\tau_1)^2}$$

$$\propto \frac{1}{r_c^3}\frac{dB_S(X)}{dX}\frac{\tau_1(\omega_n)}{1+(\omega_n\tau_1)^2} \quad , \tag{12}$$

where r_c is the wipeout radius, $\tau_1(\omega_n)$ and $\tau_2(\omega_n)$ are the longitudinal and transverse correlation times of the impurity spin at the nuclear resonance frequency, $B_S(X)$ is the Brillouin function for spin S, $X = \gamma_m \hbar SH/kT$, and the subscripts n and m refer to the nuclear and electron systems. Both the GH and BGS relaxation rates are proportional to J^2 while the LD and TD relaxation rates do not depend explicitly on J.[24]

It must be emphasized that there are several sources of uncertainty in determining the magnitude and even the field and temperature dependence of the wipeout radius r_c and the impurity-spin-correlation times. Normally, the wipeout radius is inferred from cw NMR intensity studies. It is not obvious that this same value of r_c is appropriate in these dynamic measurements. Also, it is not clear whether the values of τ_1 and τ_2 inferred from electron-spin-resonance (ESR) experiments at ω_m are the same as the values which would be effective in the nuclear relaxation at ω_n, although this does seem to be the case for the BGS relaxation rate in the strongly "bottlenecked" *Cu*Mn systems.[24] In many systems (including *Cu*Fe) ESR measurements of the correlation times are not available. In these cases, estimates of the impurity-spin-correlation times must be inferred from indirect measurements or from theoretical predictions.

The correlation times in Eqs. (10)–(12) arise from two sources. The local moment can relax to the lattice by means of the conduction electrons in a manner analogous to the Korringa relaxation of the nuclei giving a contribution to τ_1^{-1} proportional to T. In addition, there is a contribution to τ_1^{-1} from the spin-flipping rate due to interactions between the impurities. McHenry *et al.*[27] have investigated this correlation between the impurities using a short-time high-temperature expansion of the correlation function and found that τ_1^{-1} was proportional to the impurity concentration and temperature independence. They show that this term can account for the concentration dependence of τ_1 for the Al relaxation in La(Gd)Al$_2$ via the LD mechanism.[27]

In Fig. 17 we showed that the low-concentration data for *Cu*Fe in the liquid-helium-temperature range lie on a single curve when plotted as $T(cT_{1i})^{-1}$ vs T/H. Before these data can be discussed in terms of the various relaxation mechanisms, the effects caused by the variation of the wipeout number with magnetic field and temperature must be considered. The relative intensity changes in the spin-echo and the integrated cw absorption signals were measured for a 305-ppm *Cu*Fe sample for several fields and temperatures. In each case the signal intensity was found to increase by about 40% as the field decreased from 13 to 5 kOe when measured relative to pure Al powder. However, the intensity exhibited no detectable temperature dependence in the range 1.65 to 4.2 °K, in contrast to the results of Nagasawa and Steyert who reported the wipeout number to increase by a factor of 2 between 4.2 and 1.4 °K in a 380-ppm sample.[28] Their measurements were made in the dispersion mode, while the present study measured the cw absorption, but this difference should not affect the temperature dependence of the intensity.

In view of the observed field dependence of the NMR signal intensity, we will assume that n_c increases by a factor of 2 as the field increases from 2.5 to 15 kOe. (Such a variation could reflect a change from quadrupole dominance of the wipeout at the lowest fields to magnetic dominance as the field increases.[29]) The data of Fig. 17 have then been adjusted by assuming a linear increase in n_c in going from 2.65 to 15 kOe as shown in Fig. 18 for a typical alloy. The resulting plot of the relaxation data is reasonably well fit by the relation

$$T_{1i}^{-1} = 6.0\times 10^{-3} c B'_{3/2}(X)/T \quad . \tag{13}$$

As shown in Fig. 18 no fit is possible using a $B_{3/2}(X)/X$ function, suggesting that the LD mechanism [Eq. (10)] is dominant.

None of the other relaxation mechanisms have the correct field and temperature dependences if they are scaled with the impurity magnetization, i.e., $\langle S_z\rangle \propto H/(T+29)^{-1}$. But it is not clear that this is the case if the effect of the additional oscillatory spin polarization is taken into account. Since the magnitudes of the GH and BGS mechanisms scale as J^2, where J in this case should be deter-

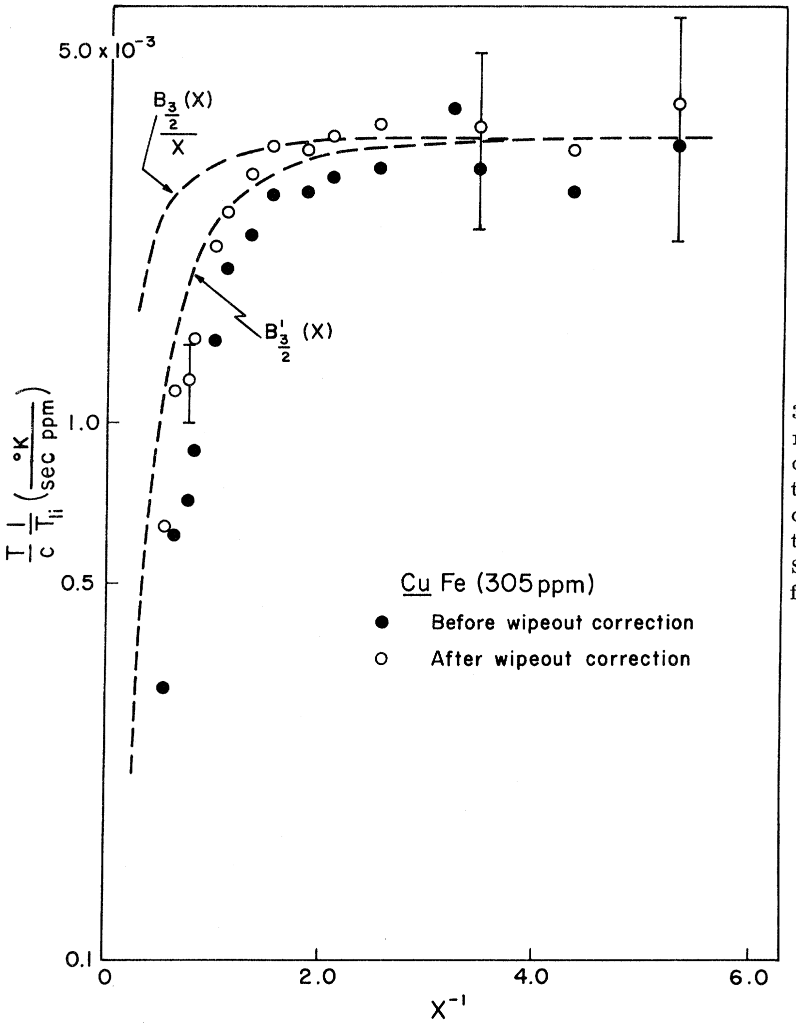

FIG. 18. $T(cT_{1i})^{-1}$vs $X=g\mu_B SH/(kT)$ for 305-ppm *Cu*Fe sample. The solid circles represent the measured T_{1i} data and the open circles represent the same data after correcting for a field-dependent wipeout number. These data are typical of all the dilute ($c<305$ ppm) *Cu*Fe samples. Shown also are $dB_{3/2}(X)/dX$ and $B_{3/2}(X)/X$ fits to the data.

mined by the *d* resonant-scattering mechanism, one might expect that the effect of the enhanced oscillatory spin polarizations could be accounted for by replacing J by

$$J \rightarrow J\left[1+(0.9/H)\int_0^H \xi(H',T)\,dH'\right] . \tag{14}$$

However, this does not improve the agreement for the field dependence of the GH or BGS mechanisms because H_c is too high to give any significant modification of the field dependence for these dilute alloys. Of course, whether the function $\xi(H,T)$ is the same at $\omega=\omega_n$ as for $\omega=0$ has not been determined.

These results suggest that the LD mechanism is dominant in this temperature range and hence valid for $T<T_K$ taking a free-spin behavior rather than the measured field and temperature dependence of $\langle S_z\rangle$. This is consistent with the observation that the LD mechanism should not be sensitive to the low-temperature correlations in the electron sea due to the Kondo effect.[24]

A comparison of Eqs. (12) and (13) show that if the LD mechanism is dominant in this temperature range, then the impurity-spin-correlation time τ_1 has a value $\tau_1^{-1}=1.1\times10^{10}T$ (sec^{-1}) (for $S=\frac{3}{2}$ and $\omega_n\tau_1\ll1$).[30] Since the Fe resonance in *Cu*Fe has not been observed, there is no direct measurement against which this value may be compared. However, the temperature dependence of τ_1 suggests that the "Korringa" term dominates any interaction term for the dilute alloys. The "Korringa" term has the form[1]

$$\tau_1^{-1}=(\pi/\hbar)J^2[N(0)/N]^2 kT . \tag{15}$$

For *Cu*Fe, $N(0)/N=0.286$ eV^{-1}atom^{-1} (for both spin directions) so that $\tau_1^{-1}=3.4\times10^{10}J^2T$ sec^{-1} which agrees with the experimental value if $J\approx0.6$ eV. This result would imply that the Korringa relaxation occurs via the *s*-*d* exchange interaction, which is typically of the order of 1 eV or less.

From the above discussion it would seem reasonable to conclude that the LD mechanism is responsible for the excess relaxation rate in the liquid-helium-temperature range. However, this identification cannot be made with any confidence considering the data for the *Cu*Fe and *Cu*Cr alloys at very low temperatures and the data of HK[14] for $T > 4.2$ °K.

Because it *appears* to be somewhat simpler and the value of T_{1i}^{-1} for $T \gg T_K$ has been more accurately determined, we will first discuss the T_1 data for the Kondo system *Cu*Cr. Gladstone[15,29] measured the Cu relaxation rate in a 30-ppm *Cu*Cr sample from 0.03 to 0.4 °K and from 2 to 10 kOe finding at the lowest fields that $T_{1i}^{-1} = 8.9 \times 10^{-2} cT$ sec^{-1} (c in ppm) for $T \ll T_K$ up to about 0.05 °K. In this temperature range, the linear dependence of T_{1i}^{-1} on T would be indistinguishable from the form $T/(T+\theta)$, where $\theta = 4.5 T_K \approx 1$ °K for *Cu*Cr, so for this temperature region we can write $T_{1i}^{-1} = 8.9 \times 10^{-2} cT/(T+1)$ sec^{-1}. Gladstone found that with increasing field and temperature $(T_{1i}T)^{-1}$ decreased rapidly. He suggested that the enhancement of $(T_{1i}T)^{-1}$ for $T \ll T_K$ might result either from a modified BGS mechanism or from an enhancement of the GH mechanism at very low temperatures. In their paper, HK[14] have shown that their T_1 data for a 100-ppm *Cu*Cr sample from 1.2 to 4.2 °K at 3.5 and 7.0 kOe can be fit by $T_{1i}^{-1} = 0.28 \times 10^{-2} cT/(T+1)$ sec^{-1} for $T > T_K$. While there appears to be a slight field dependence to their T_1 data, HK point out that the form of the GH mechanism gives the most reasonable fit to the data in this temperature range. However, the magnitude of T_{1i}^{-1} resulting from the revised GH mechanism[24] is an order of magnitude too small, even when using $J \approx 5$ eV. If the GH mechanism dominates for $T \ll T_K$ and $T > T_K$, this suggests an enhancement of T_{1i}^{-1} by a factor of 30 at low temperatures. Given the factor-of-4 enhancement observed for the NMR linewidth[3] plus the J^2 dependence of the GH mechanism, one might expect an enhancement of ~16 for the GH mechanism. Considering the uncertainties in the Cu linewidth and relaxation-rate enhancements in *Cu*Cr, this agreement is not too unreasonable.

Let us turn now to a similar consideration of existing data for the *Cu*Fe system. From the low-temperature (0.03 to 0.3 °K) measurements of Welsh *et al.* on *Cu*Fe,[16] the excess relaxation rate might be taken to be linear in c for very dilute Fe concentrations. The excess relaxation rate can then be written $T_{1i}^{-1} = 1.57 \times 10^{-2} cT/(T+29)$ sec^{-1} in this temperature range. HK[14] have measured T_1 for *Cu*Fe in the region $T > T_K$ and claim a fit to their data given by $T_{1i}^{-1} = 0.8 \times 10^{-2} cT/(T+29)$ sec^{-1} for $T > T_K$. From the scatter in their data above 4.2 °K, it is not clear that this form of the excess relaxation rate is justified. Indeed, we noted in Sec. III that our measurements permitted us to place an upper limit on the excess relaxation rate at 77 °K of $0.32 \times 10^{-2} cT/(T+29)$ sec^{-1}, which is less than half the value obtained by HK. However, if the GH mechanism in *Cu*Cr is correct, it is reasonable to assume that this might also be the case in *Cu*Fe. Note that when T_{1i}^{-1} is written in the form $T_{1i}^{-1} = KcT/(T+\theta)$, $K(Cu\text{Cr})$ and $K(Cu\text{Fe})$ are very similar in value, which would be expected if the GH mechanism is dominant and if the J values are roughly the same. If one assumes that the GH mechanism is dominant in *Cu*Fe for $T \ll T_K$ and $T \gtrsim T_K$, then the enhancement of the excess rate for $T \ll T_K$ is about 5 above the high-temperature value. From the linewidth enhancement of about 2 for $T \ll T_K$ the expected enhancement for the GH mechanism would be about 4, which is in reasonable agreement with the experimental value of $\gtrsim 5$.

An identification of the relaxation-rate mechanism as dominated by GH at high temperature ($T \gtrsim 4.2$ °K) or an enhanced-GH mechanism at very low temperature ($T \lesssim 0.3$ °K) appears to be inconsistent with the LD mechanism dominating from 1.4 to 4.2 °K. The LD mechanism is negligible for very low temperature because of the exponential decrease of this contribution in moderate fields. However, it is clear that from 1.4 to 77 °K the GH contribution would still be important although its actual contribution would be difficult to determine since, from the linewidth results discussed earlier, some enhancement of the GH mechanism might be expected in the liquid-helium temperature range.

We conclude that, while the impurity contribution to the Cu relaxation rate in *Cu*Fe alloys that we have presented appears to be best fit by the LD mechanism, it is difficult to see how this fact can be consistent with the tentative identification of a dominant GH mechanism for $T \gtrsim T_K$ made by Hanabusa and Kushida.[14] It is possible that the fit of T_{1i}^{-1} to a $B'_{3/2}(X)$ function is fortuitous, and the strong-field dependence of our data results from the effects of enhanced spin correlations in the Kondo state although this would not be expected from the value of $\xi(H, T)$ for the magnetic fields used in the relaxation measurements. An alternate hypothesis, of course, is that none of the mechanisms discussed here correctly describe the impurity contribution to the host relaxation rate below the Kondo temperature, and that the correct theoretical treatment of this problem has yet to be presented.

V. CONCLUSIONS

In this paper we have presented a detailed experimental study of the concentration, magnetic field, and temperature dependences of Cu^{63} NMR linewidth and spin-lattice relaxation time in very dilute *Cu*Fe alloys. The data presented here have led us to several conclusions which are essential to understanding the magnetic properties of *Cu*Fe at temperatures less than the Kondo temperature. The impurity contribution to the host NMR linewidth, which reflects the spatially oscillating conduction-electron-spin polarization induced by the impurity, shows a rapidly increasing slope with decreasing applied field below a critical field H_c and a similar increase with decreasing temperature below the Kondo temperature. This behavior is found to increase linearly with increasing Fe concentration over the entire range studied ($90 < c < 1260$ ppm). We have concluded that we are observing the effects of single Fe impurities rather than magnetic Fe pairs or clusters. Such an effect was first observe by Heeger *et al.*[3] and interpreted by Golibersuch and Heeger[4] in terms of the relatively localized "quasiparticle"-spin-polarization cloud concept suggested by the Applebaum-Kondo formulation of the Kondo problem.[21] This interpretation, which was supported by the existing susceptibility data, suggested an enhanced single-impurity contribution to the susceptibility in moderate fields at low temperatures. However, the more recent magnetization measurements of Tholence and Tournier[6] indicate that no concurrent enhancement of the single-impurity susceptibility occurs at low temperature indicating that no net spin polarization results from the additional oscillatory spin polarization around an Fe impurity in the Kondo state. Our results show that the (perturbative) oscillatory spin polarization, which is known to exist for $T \gg T_K$, is enhanced at low temperatures as a result of the many-body correlations between the conduction electron and impurity spins. This extra oscillatory spin polarization saturates out over a relatively narrow-field range with increasing applied field. We have found that, in the infinite dilution limit ($c \to 0$), an applied field between 30 and 60 kOe is required for saturation. Similarly, increasing thermal energy breaks up this extra oscillatory spin polarization so that the enhancement decreases to half its low-temperature value at a temperature of about 6 °K, which is essentially the value of T_K. Our measurements have enabled us to trace out the intrinsic field and temperature dependence of this additional oscillatory spin polarization, at least insofar as it is reflected in the static ($\omega = 0$) NMR linewidths. This field and temperature profile is expressed by the function $\xi(H, T)$.

The applied field H_c at which the extra low-field oscillatory spin polarization saturates, varies in inverse proportion to the Fe concentration for constant temperature. This fact, along with the concentration independence of ΔH at H_c, indicates the existence of large effective fields in *Cu*Fe arising from the long-range indirect coupling between Fe impurities. Effective fields of the required magnitude probably arise from the *d-d* double-resonance scattering mechanism.

Our measurements of the host nuclear relaxation rate in these *Cu*Fe samples have shown that the impurity-induced rate is strongly enhanced between 4.2 and 1.4 °K, and decreases rapidly with increasing applied field between 2.5 and 15 kOe. The excess rate varies linearly with the Fe concentration up to about ~400-ppm Fe at all applied fields. The data for concentrations less than ~400 ppm were shown to lie on a single curve when plotted as $T(cT_{1i})^{-1}$ vs T/H. Taken alone, these data would imply that the relaxation in this temperature range is dominated by a dipole-dipole coupling of the nuclei to longitudinal fluctuations of the impurity spin. This identification would lead to an estimate for the impurity-spin correlation time τ_1 which is in reasonable agreement with the expected value of τ_1 resulting from the *s-d* exchange interaction.

However, the apparent agreement of the relaxation data with the longitudinal dipolar mechanism may be somewhat fortuitous. A comparison of the systems *Cu*Fe and *Cu*Cr indicates that relaxation data for $T > T_K$ may be consistent with a mechanism in which the nuclei relax via a virtual excitation of the impurity spin mediated by the conduction electrons. This possibility precludes a conclusive identification of a single-relaxation mechanism in the liquid-helium-temperature region. As a result it is not clear that any of the $T > T_K$ relaxation processes may be simply extended to the temperature range $T < T_K$.

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Nuclear-Magnetic-Resonance Study of Tightly Pinned Domain Walls in α-Fe_2O_3

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Fe^{57} NMR in α-Fe_2O_3 is used to determine the behavior of tightly pinned domains in a static magnetic field. The predominant positive-phase component of the NMR signal is found to be due to strongly pinned domains with ~180° antiferromagnetic walls. A model wherein domains are nucleated about local-strain axes is proposed to explain the observed behavior. Finally, a possible explanation of the anomalous temperature dependence of the spontaneous moment reported by Searle and Dean is suggested.

INTRODUCTION

Hematite is basically an antiferromagnet with a weak spontaneous moment which appears because of a slight canting of the sublattice magnetizations toward one another via the Dzialoshinski-Moriya canting interaction and, therefore, some interesting domain configurations might be expected. A domain structure was first detected in hematite by Blackman *et al.*,[1] and since this time several workers have tried to establish exactly what type of domain structure is present in this material.[2-6] The various techniques that have been used to this end include neutron diffraction, the Faraday effect, and the Bitter technique.

Recent nuclear-magnetic-resonance (NMR) studies by Hirai *et al.*[7] suggest that the NMR signals in α-Fe_2O_3 originate in domain walls. This observation has been put on strong experimental grounds by Maartense and Searle,[8] who directly detected a domain-wall resonance predicted by Hirai *et al.*[7]

The nuclear-resonance frequency for an individual nucleus depends on the projection of the applied field $\vec{H}_0$ on the direction of the hyperfine field $\vec{H}_{hf}$ at the nucleus, as long as $|\vec{H}_0| \ll |\vec{H}_{hf}|$. The angular distribution of $\vec{H}_{hf}$ with respect to $\vec{H}_0$ through the domain wall is expected to be sensitive to the wall structure. Thus, since the NMR signals originate in domain walls, the behavior of the