Experimental Study of the Low-Temperature Spin Correlations in the Magnetic-Impurity Problem*†

D. C. GOLIBERSUCH‡ AND A. J. HEEGER§
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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In an attempt to verify the existence of the extended spin-polarization cloud associated with the ground state of the magnetic-impurity problem, we have presented results of a new set of NMR experiments together with a review of the Mössbauer and bulk-susceptibility data on *Cu* Fe. The results demonstrate the existence of the quasiparticle polarization cloud in this system. Analysis of the published Mössbauer and bulk-susceptibility data demonstrates that the local *d*-spin susceptibility accounts for only one-half of the total susceptibility for $T \ll T_K$. From a study of the nuclear-resonance linewidth data we see that the remainder of the susceptibility is located in a spatially extended spin-polarization cloud around the impurity sites. By a model-independent analysis of the data, we obtain a measure of the temperature and magnetic-field dependence of the amplitude of the quasiparticle. In addition, the NMR linewidth studies are extended to magnetic fields as low as 170 G. At fields below 3 kG, a strong field dependence is observed which is attributed to the presence of very small amounts of precipitated Fe in the form of superparamagnetic clusters.

I. INTRODUCTION

Considerable experimental effort has been directed toward a more complete understanding of the ground state of a "magnetic" impurity interacting with the conduction electrons of a metal via an isotropic *s-d* exchange interaction. The experiments are, in those cases studied in detail,[1] generally consistent with the theoretical concept of a local-moment–conduction-electron many-body singlet state. There remains, however, some uncertainty in the nature and range of the ground-state spin correlations in the conduction-electron sea in the vicinity of such an impurity. It seems clear that at least within the *s-d* model, such spin correlations will be important only at temperatures sufficiently low that the thermal energy is small or at least comparable with the spin-correlation energy $\epsilon_B \equiv kT_K$. This follows simply from the observation that a perturbative treatment for the calculation of the magnetic susceptibility is valid at high temperature ($T > T_K$), whereas the ground state of the problem is known to be a many-body singlet.[2] One can thus argue quite generally that these low-temperature spin correlations in the electron gas will be spatially extended since they must be formed from conduction-electron states within $\Delta k \sim (kT_K/E_F)k_F$ of the Fermi surface (these are the only states available for such a low-energy phenomenon) and therefore, have a range of the order $\xi_0 \simeq [(kT_K/E_F)k_F]^{-1}$.

One can indeed question the validity of the *s-d* model itself. However, Schrieffer and Wolff[3] have shown that the *s-d* Hamiltonian can be derived directly from the somewhat more fundamental Anderson Hamiltonian[4] in the limit when the ratio of the virtual level width Γ to the Coulomb repulsion U is small. This ratio is experimentally in the range 0.1–0.2 in the case of transition metal impurities in the simple metals[5–9] so that the *s-d* Hamiltonian (with appropriate momentum dependence included) should provide a reasonable description of the physics of the problem. Recent work on the impurity problem from the point of view of spin fluctuations[10] has indicated that the concept of a well-defined localized spin with *infinite* lifetime is never valid (except possibly in the infinite U limit). However, if the spin-fluctuation lifetime is sufficiently long, the *s-d* model will be appropriate and the above arguments on extended spin correlations valid. The corresponding situation in the case of a short spin-fluctuation lifetime is at present less well understood since the spatial dependence of the electron-gas correlations has been averaged out from the beginning.[10] Clearly, experimental data on a variety of systems is needed to clarify the situation and provide a guide for further theoretical work.

In this paper, we present and summarize the data for a particular system, dilute solutions of Fe in Cu metal: and show that these data imply the existence of spatially extended spin correlations which build up continuously with decreasing temperature for $T < T_K$. By comparing the bulk-susceptibility results with the Mössbauer data

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‡ Part of this work supported by a National Aeronautics and Space Administration predoctoral fellowship.

§ John Simon Guggenheim Fellow, 1968–1969.

[1] M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. **40**, 380 (1968).

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[3] J. R. Schrieffer and P. Wolff, Phys. Rev. **149**, 491 (1966).

[4] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[5] A. P. Klein and A. J. Heeger, Phys. Rev. **144**, 458 (1966).

[6] J. A. McElroy and A. J. Heeger, Phys. Rev. Letters **20**, 1481 (1968).

[7] J. A. Gardner and C. P. Flynn, Phys. Rev. Letters **17**, 579 (1966).

[8] H. P. Myers, L. Walden, and A. Karlsson, Phil. Mag. **18**, 725 (1968). By means of spectroscopic and photoemission studies, Myers and co-workers have been able to directly determine the spin splitting of the virtual levels of Mn in Ag as 5 eV.

[9] S. Tomaki, J. Phys. Soc. Japan **22**, 865 (1967).

[10] M. Levine and H. Suhl, Phys. Rev. **171**, 567 (1968).

we demonstrate that approximately one-half the total low-temperature susceptibility resides locally on the impurity site, the remainder being distributed in a spatially extended polarization cloud about the impurity. The properties of this spin-polarization cloud have been studied via measurements of the nuclear magnetic resonance linewidth of the host-metal nuclei. The results provide information on the second and higher moments of the quasiparticle polarization and imply the existence of relatively long-range spin correlations in the electron gas.

Although we shall attempt to analyze the data generally in a manner independent of any particular model, it is useful to have in mind some theortical results as an aid to unraveling the various aspects of the data. Moreover, we will attempt to make a comparison of theory and experiment where possible. We choose to use the theory of Appelbaum and Kondo[11] as a guide because it is conceptually simple, and, more important, it is the only theory worked out in sufficient detail to give the needed information on the susceptibility and conduction-electron spin polarization. Appelbaum and Kondo introduced the trial ground-state wave function

$$|G\rangle=(1/\sqrt{2})(a_{0\uparrow}{}^{+}\beta-a_{0\downarrow}{}^{+}\alpha)a_{l\uparrow}{}^{+}a_{l\downarrow}{}^{+}|vac\rangle. \qquad (1)$$

The creation operator $a_{0\sigma}{}^{+}$ creates a quasiparticle which is coupled into a singlet with the impurity (with spin wave functions α and β) in the presence of the self-consistently determined Fermi sea built up from scattering states $a_{l\sigma}{}^{+}$ (for details see Refs. 11 and 12). In their paper, Appelbaum and Kondo showed that the above trial function was the exact eigenstate of a part of the Hamiltonian H_0 with a binding energy

$$\epsilon_B\equiv kT_K=D\exp(-1/3J\rho), \qquad (2)$$

relative to the free Fermi sea. In the above, ρ is the density of states in a flat band of width $2D$ centered on the Fermi surface, and J is the *s-d* exchange coupling constant. Recent work[13] has shown that treatment of the remainder of the Hamiltonian by perturbation theory leads to additional terms nonanalytic in $J\rho$, thereby implying that the concept of an *infinite lifetime* quasiparticle is invalid. (With hindsight, this is obvious for if the quasiparticle were to have an infinite lifetime, the problem would be a one-electron problem and easily solved.) However, the validity of the quasiparticle concept with a finite lifetime is a possibility worthy of further study.

The magnetic susceptibility and spin polarization around a partially magnetized impurity in an external magnetic field have been worked out by Heeger, Welsh, Jensen, and Gladstone[12] within the framework of the Appelbaum-Kondo theory. The resulting expression for the susceptibility is

$$\chi_{\text{total}}=\chi_{\text{Pauli}}+\chi_{\text{loc}}+\chi_Q, \qquad (3)$$

where χ_{Pauli} is the usual Pauli susceptibility of the free-electron gas, and

$$\chi_{\text{loc}}=\chi_Q=\mu^2/[\tfrac{4}{3}\,kT_K\ln(D/kT_K)]. \qquad (4)$$

The spin polarization around the partially magnetized impurity is given by

$$\sigma(r)=\sigma_0+\sigma_{\text{RKKY}}(r)+\sigma_Q(r), \qquad (5)$$

where σ_0 is the uniform polarization due to the external field, $\sigma_{\text{RKKY}}(r)$ is the usual RKKY term[14]

$$\sigma_{\text{RKKY}}(r)\propto\langle S_z\rangle(\cos 2k_Fr)/r^3, \qquad (6a)$$

and $\sigma_Q(r)$ is the quasiparticle term

$$\sigma_Q(r)\propto\langle S_z\rangle[(\sin k_Fr)/r]^2. \qquad (6b)$$

The above expression is valid only at $T=0$°K. One expects that with increasing temperature and magnetic field the spin correlations associated with the ground state will gradually break up and the quasiparticle amplitude will continuously decrease. There are two important features of the above expressions to be emphasized: (1) Since $\chi_{\text{loc}}=\chi_Q$, the local susceptibility (localized on the impurity site) would be one-half of the experimentally determined added susceptibility per impurity at $T=0$°K. (2) $\sigma_Q(r)$ is a long-range oscillatory, but positive-definite function with a range of order $\xi_0=[(kT_K/E_F)k_F]^{-1}$.

In Sec. II, we describe the NMR experiments. This is followed in Sec. III by an analysis of the Mössbauer and bulk-susceptibility data from which we obtain the temperature dependence of χ_{loc}. We are then in a position in Sec. IV to analyze the NMR data. An extra contribution to the linewidth is found at low temperatures, and from this we obtain the temperature and field dependence of the quasiparticle amplitude. In Sec. V, we discuss the apparently extraneous very-low-field (<3 kG) data.

II. NMR EXPERIMENTS

The conduction-electron spin polarization around a magnetic impurity will interact via the hyperfine interaction with the host nuclei surrounding the impurity. The nuclear magnetic resonance of the host will thus be subject to an inhomogeneous Knight-shift broadening. Sugawara[15] has discussed a limited study of this effect for two *Cu*Fe samples (0.04 and 0.11 at.%). In this section, we describe a new and considerably more detailed study of the temperature and field dependence of the Cu^{63} NMR for a CuFe$_{0.048}$ sample. These detailed results were required in order to clearly demonstrate experimentally the existence of the low-temperature

[11] J. A. Appelbaum and J. Kondo, Phys. Rev. Letters **19**, 906 (1967); Phys. Rev. **170**, 524 (1968).

[12] A. J. Heeger, L. B. Welsh, M. A. Jensen, and G. Gladstone, Phys. Rev. **172**, 302 (1968).

[13] D. Hamann (private communication).

[14] For a discussion, see C. Kittel, *Quantum Theory of Solids* (Wiley-Interscience, Inc., New York, 1961), p. 360.

[15] T. Sugawara, J. Phys. Soc. Japan **14**, 643 (1959).

spin correlations in the electron gas which are the subject of this paper.

The sample used for these new data was prepared from 99.999% Cu and 99.99% Fe. The constituents were melted in a high-vacuum tantalum heating-element furnace in a high-purity alumina boat (90×7×11 mm) and held at 1200°C for 2 h. The approximately 100-g sample was then cooled under flowing He gas. After removal from the crucible, the alloy was thoroughly etched in HNO_3, sealed in an evacuated quartz tube, annealed at 950°C for 3 days, and finally, rapidly quenched in water. We have observed that a sample prepared in this manner results in a homogeneous alloy, at least on a macroscopic scale. This observation is based on the fact that the NMR linewidths for material taken from opposite ends of such a sample are identical. Further, the results of chemical analysis are the same for different samplings of the alloy ingot. The weighed constituents were such as to produce a 0.049 at.% Fe alloy. Chemical analysis indicated 0.048 at.% Fe. In addition, as a check on the unintentional introduction of additional impurities, a spectroscopic analysis was performed. The only impurities observed other than the Fe were Si(0.00X at.%) and Ag(0.000X at.%).[16]

The sample was then mechanically filed; the filings were passed through a 400-mesh sieve, and subsequently, magnetically cleaned. Microscopic examination indicated that the particles so obtained were roughly spherical to cylindrical in shape with the smallest dimension in a range from 5 to 40 μ with a mean of 20 μ. This is to be contrasted with the work of Sugawara[15] in which the samples were prepared so as to yield particles of less than 2-μ size. With the corresponding large surface area to volume ratio for such small particles one could expect the well-documented effect of internal oxidation[17] of transition element impurities in Cu to be highly accelerated. In fact, our data are generally consistent with that of Sugawara only if his reported concentration values are reduced by 60%. In addition, there is a possible problem related to the suspected long range of the low-temperature spin correlations which are the subject of this paper. Various theoretical treatments[11,12,18] have indicated a coherence length as great a 7000 Å for Fe in Cu while recent examinations[12] of the experimental data suggest that 1000 Å is closer to reality. Taking the lower figure we find that, for a 1-μ particle, 50% of the Fe impurities are within a coherence length of the surface. For a 20-μ particle, 25% of the impurities will be within 1000 Å of the surface. For reasons of convenient preparation as well as to minimize the above two effects, the 400-mesh particles would seem ideal.

On the other hand, with particles of this size one must resolve the question of possible eddy-current effects. The classical skin depth in microns is $\delta = 50(\rho/\nu)^{1/2}$, where ρ is the resistivity in μΩ cm and ν the frequency in MHz. For *Cu*Fe, the residual resistivity is approximately 13 μΩ cm per at.% of Fe.[19–22] Thus CuFe$_{0.05}$ at low temperatures (<4°K) and a frequency of 10 MHz will have a skin depth of 13 μ. This is to be compared with an average minimum diameter particle size of 20 μ. Bloembergen[23] and Chapman, Rhodes, and Seymour[24] analyzed the effect in terms of an admixture of absorption χ'' and dispersion χ' components of the susceptility. They show that the derivative of the observed signal will be given by

$$g(H) = (d/dH)[\chi''(H) + \alpha\chi'(H)]. \tag{7}$$

A useful operational measure of the degree of admixture is given by the ratio $y_1/(y_1+y_2)$, where y_1 and y_2 are defined in Fig. 1. This ratio never exceeded 0.53 in the present experiments. For a Lorentzian curve, this corresponds to an admixture $\alpha = 0.14$. Chapman *et al.*[24] find that for a particle diameter to skin depth ratio $d/\delta = 1.5$ that $\alpha = 0.25$ for a cylindrical particle and $\alpha = 0.1$ for a spherical particle in good agreement with our observations. In this investigation, we have measured the peak-to-peak width of the derivative curve ΔH_p as well as the "wing" width ΔH_2 defined in Fig. 1. Graphical analysis of $g(H)$ with $\alpha = 0.12$ shows that the measured values of ΔH_p and ΔH_2 deviate from the values for a pure absorption derivative curve by less than 1.5%. This deviation is well within the experi-

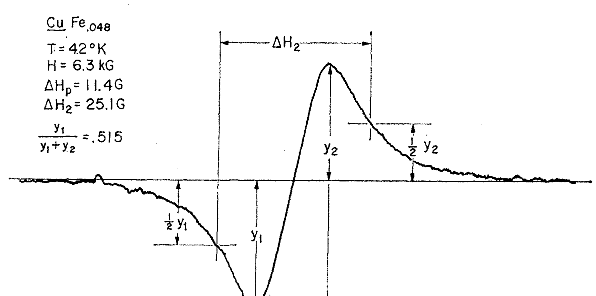

FIG. 1. Tracing of the Cu^{63} nuclear magnetic resonance line for CuFe$_{0.048}$ at 4.2°K. The quantities y_1 and y_2 define the symmetry of the line. The peak-to-peak linewidth ΔH_p and the wing width ΔH_2, at which point the signal is reduced to one-half maximum, are shown.

[16] Elements checked but not found: Sb, As, Ba, Be, Bi, B, Cd, Nb, Ga, Ge, Au, Mo, P, Pt, K, Sr, Te, W, V, Zr, Al, Ca, Cr, Co, Pb, Mg, Mn, Ni, Na, Sn, Ti, and Zn.

[17] D. H. Howling, Phys. Rev. **155**, 642 (1967).

[18] A. J. Heeger and M. A. Jensen, Phys. Rev. Letters **18**, 485 (1967).

[19] M. D. Daybell and N. A. Steyert, Phys. Rev. Letters **18**, 390 (1967).

[20] A. Kjekshus and W. B. Pearson, Can. J. Phys. **40**, 98 (1961).

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[22] G. K. White, Can. J. Phys. **33**, 119 (1955).

[23] N. Bloembergen, J. Appl. Phys. **23**, 1383 (1952).

[24] A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) **70**, 345 (1956).

mental measurement error of 5–10% and consequently has been ignored.

The signal was detected using the circuit of Robinson.[25] Because of the frequency range covered, it was necessary to use three separate coils: 80 μH from 260 kHz to 2.3 MHz, 4.4 μH from 3.6–6.8 MHz, and 1 μH from 7.1–13.6 MHz. The rf level was adjusted to optimize signal to noise and maintain $\gamma^2 H_1^2 T_1 T_2 \ll 1$. Peak-to-peak field modulation of 2.5 G at 250 Hz was employed.

Temperature control between helium and nitrogen temperatures was achieved using a modification of the "dunut"[26] scheme shown schematically in Fig. 2. Temperature was measured below 4.2°K with reference to the standard helium-vapor pressure tables between 4.2 and 10°K by a 1-$k\Omega$ Alden-Bradley carbon resister and at 10°K and above by a copper-constantan thermo-

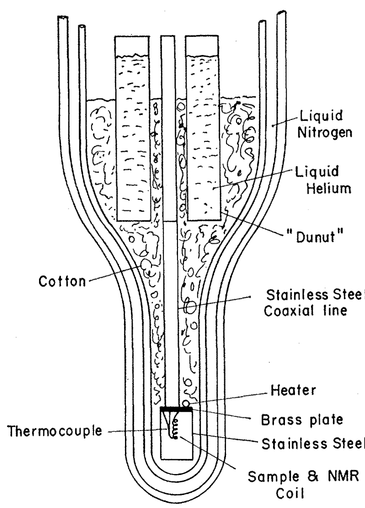

FIG. 2. Schematic drawing of the low-temperature apparatus. The sample, thermocouple, and heater were thermally bonded with Apiezon grease. The cotton reduced excessive convection cooling.

couple. Deviation about a desired temperature was observed on the null detector of a potentiometer, and the heater power manually adjusted to counteract the drift. Using this simple scheme, it was possible to hold a desired temperature within 0.5°K for about an hour. The limit was imposed by the small 1-l capacity of the "dunut." The thermocouple was calibrated against the data of Powell, Bunch, and Corruccini[27] at 4.2 and 77.4°K. Absolute accuracy was ± 1°K for the 10°K point and considerably better for all other temperatures.

The field dependence of the NMR linewidth was examined at 14 different temperatures. In Figs. 3 and 4, we present representative examples of the data for three

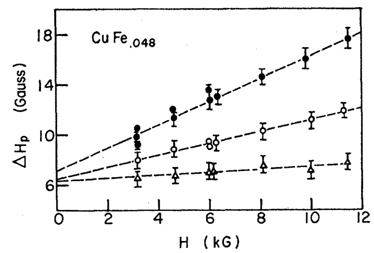

FIG. 3. Raw data showing the magnetic-field dependence of the Cu[63] peak-to-peak linewidth ΔH_p in CuFe$_{0.048}$ at representative temperatures of 2.4°K(•), 15°K(0), and 120°K(Δ).

temperatures. The error bars are estimates of measurement inaccuracies resulting from the flatness of the derivative peaks and noise. In all cases, the linewidths were linear within the experimental error for fields between 3 and 12 kG. The very-low-field data (<3 kG) will be discussed in Sec. IV.

As mentioned above, the observed linewidth results from an inhomogeneous Knight-shift broadening of the pure Cu line and may be represented by

$$g_{\text{obs}}(H)=\int_{-\infty}^{\infty} g_h(H-H')g_i(H')dH' , \qquad (8)$$

where $g_{\text{obs}}(H)$ is the measured line shape, $g_h(H)$ is the intrinsic line shape of the Cu host, and $g_i(H)$ represents the distribution of local magnetic fields due to the iron impurities. Sugawara[15] has numerically evaluated $\Delta H_p{}^i$ and $\Delta H_2{}^i$ for the derivative line shape dg_i/dH in terms of the observed widths under the assumption that $g_i(H)$ has a Lorentzian shape.[28] Using these results, we have extracted $\Delta H_p{}^i$ and $\Delta H_{p2}{}^i \equiv \Delta H_2{}^i/2.4$ from the raw data. The factor of 2.4 is such that if $g_i(H)$ is truly Lorentzian one will find that

$$\Delta H_p{}^i = \Delta H_{p2}{}^i .$$

Representative results are displayed in Figs. 5 and 6 in which the solid lines derive from a least-squares deter-

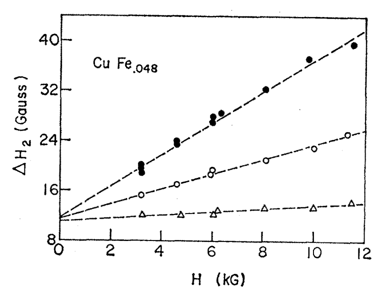

FIG. 4. Raw data showing the magnetic-field dependence of the Cu[63] wing linewidth ΔH_2 in CuFe$_{0.048}$ at 2.4°K(•), 15°K(0), and 120°K(Δ).

[25] F. N. H. Robinson, J. Sci. Instr. **36**, 481 (1959).
[26] R. E. Pontinen and T. M. Sanders, Jr., Rev. Sci. Instr. **37**, 1615 (1966).
[27] R. L. Powell, M. D. Bunch, and R. J. Corruccini, Cryogenics **1**, 139 (1961).

[28] The cut-off Lorentizan nature of $g_i(H)$ for CuMn has been carefully confirmed by Sugawara (see Ref. 15). Throughout this paper we point out those aspects of the data which confirm this assumption for CuFe.

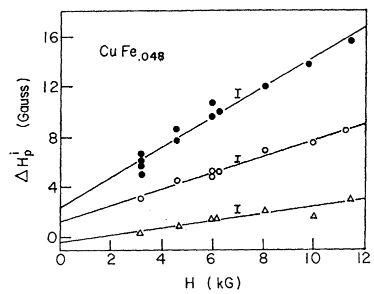

FIG. 5. The impurity contribution to the linewidth ΔH_p^i derived from the data of Fig. 3. The solid line represents a least-squares determination of the slope and intercept.

mination of the slope and intercept. A similar analysis of the NMR data was performed for each of the temperatures studied (see Figs. 13 and 14).

Before such data can be analyzed in any detail in terms of the dependence of the conduction-electron spin polarization on temperature and magnetic field, it is necessary to have detailed information on the local susceptibility, i.e., $\langle S_z^{\mathrm{Fe}}\rangle$.

III. MÖSSBAUER ANALYSIS

In this section, we analyze the available data on the hyperfine field at the Fe^{57} nucleus in *Cu*Fe and compare the results with bulk-susceptibility measurements. Our goal is to obtain information on the local susceptibility, i.e., that part of the added susceptibility per impurity which is localized on the impurity site. The hyperfine field at the Fe^{57} nucleus is proportional to $\langle S_z^{\mathrm{Fe}}\rangle$ and can be used as a measure of this local susceptibility. This relationship has been verified in a variety of metallic systems where the temperature-dependent contribution to the susceptibility from the d shell is dominant. The proportionality constant, i.e., the hyperfine field per spin is made up of several contributions (core polarization of the 1S, 2S, and 3S wave functions) but is basically determined by the electronic structure of the atom in the metal,[29] and is therefore expected to be temperature-independent.

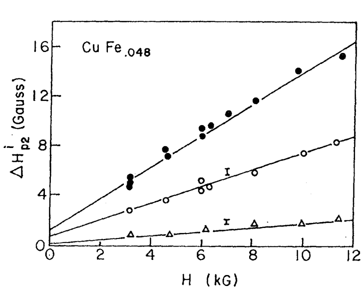

FIG. 6. The impurity contribution to ΔH_{p2}^i derived from the data of Fig. 4. The solid line represents a least-squares determination of the slope and intercept. The agreement in magnitude with Fig. 5 supports the assumption that the local magnetic-field distribution $g_i(H)$ is Lorentzian.

[29] R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), Chap. 2.

Previous analyses[30–32] of the Mössbauer data have attempted to obtain the saturation hyperfine field (i.e., the hyperfine field for the Fe spin fully saturated in a magnetic field) by fitting the data to a spin-$\frac{3}{2}$ Brillouin function. Such a procedure is subject to serious error since it is known that the susceptibility is not described by free-spin behavior even at temperatures very high compared to T_K.[33–35] Moreover, such an analysis is unnecessary since at high temperatures $\langle S_z^{\mathrm{Fe}}\rangle$ may be obtained directly from the measured bulk susceptibility and then compared with the Mössbauer splitting at the same temperature. For $T>T_K$, there is no ambiguity in $\langle S_z^{\mathrm{Fe}}\rangle$ as obtained from the bulk susceptibility, for a perturbative treatment of the problem is valid and the induced conduction-electron polarization is small ($\langle\sigma_z\rangle_p = J\rho(0)\langle S_z^{\mathrm{Fe}}\rangle$)[34] and can be neglected. Furthermore, this contribution to $\langle\sigma_z\rangle$ will be present at all temperatures as its origin is in the perturbative scattering of the conduction electrons from the self-consistently determined value of $\langle S_z^{\mathrm{Fe}}\rangle$ via the s-d exchange. This perturbative contribution is not affected by the existence of the many-body condensed state at low temperatures which involves only the very-low-energy part of the s-d Hamiltonian (of order kT_K about the Fermi surface). As a result, any contribution of $\langle\sigma_z\rangle_p$ to the hyperfine field at the Fe will not affect the proportionality between the hyperfine field and $\langle S_z^{\mathrm{Fe}}\rangle$.

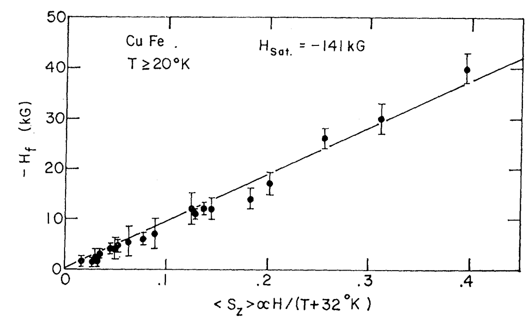

FIG. 7. The hyperfine field $|H_f|$ as measured by Mössbauer effect for dilute Fe^{57} in Cu as a function of $\langle S_z^{\mathrm{Fe}}\rangle$ at temperature $T>20$°K. The values for $\langle S_z^{\mathrm{Fe}}\rangle$ are obtained from Hurd's magnetic susceptibility data. The solid line represents a least-squares analysis of the data. The slope yields a value for the hyperfine field per spin of 94 kG.

In Fig. 7, we plot the hyperfine field at the Fe^{57} nucleus for temperatures $T>20$°K as a function of $\langle S_z^{\mathrm{Fe}}\rangle$ as obtained from the data of Hurd.[33] The hyperfine field values include data from the work of Kitchens,

[30] R. B. Frankel, N. A. Blum, B. B. Schwartz, and D. J. Kim, Phys. Rev. Letters **18**, 1050 (1967).
[31] T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. **138**, A467 (1965).
[32] M. D. Daybell and W. A Steyert, Phys. Rev. **167**, 536 (1968).
[33] C. M. Hurd, J. Phys. Chem. Solids **28**, 1345 (1967).
[34] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 505 (1965).
[35] D. J. Scalapino, Phys. Rev. Letters **16**, 937 (1966).

Steyert, and Taylor[31] as well as that of Frankel, Blum, Schwartz, and Kim.[30] We note that the susceptibility may be fit with the expression

$$\chi=\mu_{\text{eff}}^2/3k(T+32)\,,\quad \text{where}\quad \mu_{\text{eff}}=3.68\mu_B\,, \tag{9}$$

so that

$$\langle S_z^{\text{Fe}}\rangle=(1/g\mu_B)[\mu^2{}_{\text{eff}}H/3k(T+32)]\,. \tag{10}$$

Assuming $g=2$, the proportionality of the hyperfine field and $\langle S_z^{\text{Fe}}\rangle$ for $T>T_K$ is demonstrated in Fig. 7. (The solid line represents a least-squares analysis of the data.) The value of the hyperfine field per spin is found to be

$$|H_f|/\langle S_z^{\text{Fe}}\rangle=94\text{ kG} \tag{11}$$

(or a saturation hyperfine field of $H_{\text{sat}}=-141$ kG assuming spin $\frac{3}{2}$). This value is considerably larger than that estimated by other authors.[30–32] However, the determination of $H_f/\langle S_z^{\text{Fe}}\rangle$ directly from the data should give the most accurate result.

Having obtained the hyperfine field per spin, one can directly compare the low-temperature ($T\ll T_K$) Mössbauer and susceptibility data. The low-temperature susceptibility of *Cu*Fe has been studied by Daybell and Steyert[32] and is given by

$$\chi=\mu_{\text{eff}}^2/3kT_K\,, \tag{12}$$

with $\mu_{\text{eff}}^2=3.68\ \mu_B$ and $T_K=18°\text{K}$. The anomalous low-field (<1 kG) susceptibility found by Daybell and Steyert[32] is not included in the present analysis, since all the Mössbauer data were taken at fields much greater than 1 kG. In Fig. 8, we show the low-temperature Mössbauer results of H_f versus applied field. Using the hyperfine field per spin of Eq. (11), the dashed line is the result expected if the entire susceptibility of Eq. (12) is assumed localized on the impurity site, and the dash-dot line is the result if half the susceptibility is localized. The first assumption is in clear disagreement with the experimental results. Thus, the low-temperature hyperfine data imply that only 0.56 of the low-temperature susceptibility contributes to the local hyperfine field. In other words, approximately one-half of the low-temperature susceptibility is to be associated with spatially extended spin density which is primarily outside the impurity unit cell. This result is in agreement with the prediction based on the Appelbaum-Kondo singlet as discussed in Sec. I.

There is an alternative explanation of the above data, namely, that the extra susceptibility is localized but does not contribute to the hyperfine field. Watson[36] has argued that the spin polarization at the origin due to *s-d* admixture should be small. However, a precisely zero contribution to the hyperfine field from such a very large contribution to the susceptibility seems out of the question. Moreover, we shall see in Sec. IV, that such an

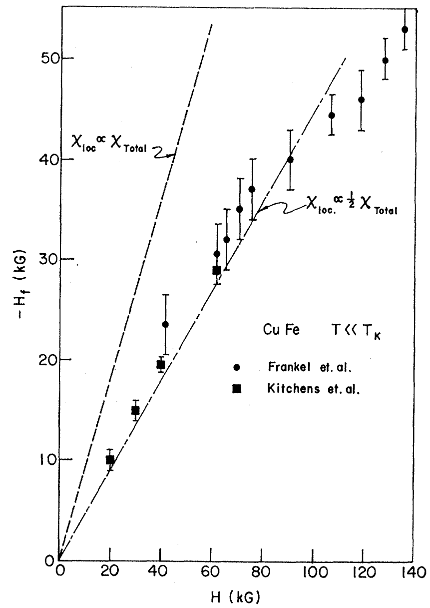

FIG. 8. The Fe^{57} hyperfine field $|H_f|$ as a function of magnetic field for $T\ll T_K$. The dashed line results from the assumption that the entire susceptibility measured (above 1 kG) at low temperatures is localized on the Fe site. The dot-dash line is the result if only half the susceptibility is assumed localized. Both lines assume the value 94 kG per spin for the hyperfine field as obtained from Fig. 7.

assumption is inconsistent with the nuclear-resonance data.

In Fig. 9, we replot the measured hyperfine fields as a function of $H/(T+32)$ including all the Mössbauer data for all temperatures. The results imply that for $\langle S_z^{\text{Fe}}\rangle<0.4$, the hyperfine field is proportional to $H/(T+32)$ to within a few percent accuracy at all temperatures including $T\ll T_K$. The low-temperature data appear to fall consistently a few percent above that for higher temperatures. This is shown more clearly in Fig. 10, where the ratio of hyperfine field to applied

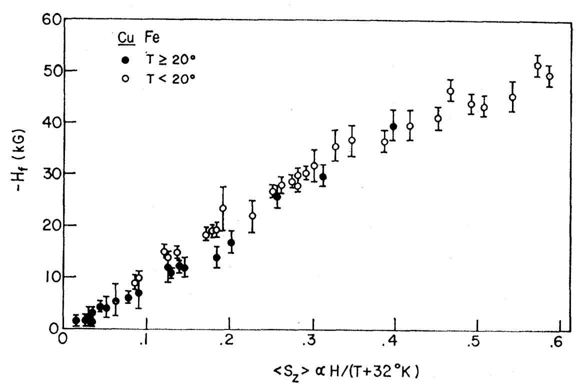

FIG. 9. The Fe^{57} hyperfine field for dilute *Cu*Fe versus $\langle S_z^{\text{Fe}}\rangle$ including all available data for temperatures. The results indicate that for $\langle S_z^{\text{Fe}}\langle<0.4$, $|Hf|$ is proportional to $H/(T+32)$ to within a few percent accuracy at *all* temperatures; including $T<T_K$.

[36] R. E. Watson, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), p. 445.

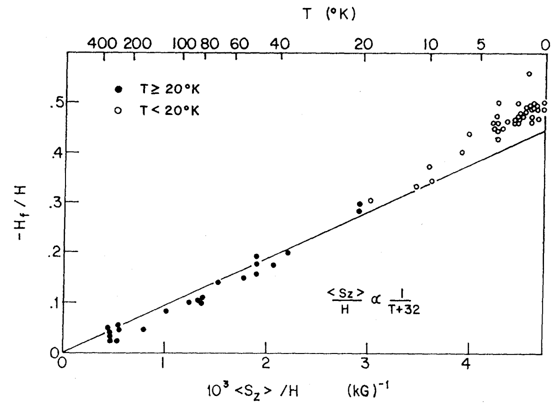

FIG. 10. $|H_f|/H$ versus $\langle S_z^{Fe}\rangle/H$ including all available *Cu*F data for $\langle S_z^{Fe}\rangle<0.4$. The small ($\sim$10%) upturn at the lowest temperature is noted.

field is plotted as a function of $\langle S_z^{Fe}\rangle/H$. The solid curve represents the same least-squares fit calculated in reference to Fig. 7. The results imply that

$$\chi_{loc} \propto \langle S_z^{Fe}\rangle/H \propto 1/(T+32)$$

to an accuracy of better than 10% at all temperatures. The deviation from the straight line at the lowest temperatures represents either a small increase in the local susceptibility or a small increase in the hyperfine coupling constant. It is impossible to conclude which of these alternatives is correct on the basis of the data alone, although a small increase in χ_{loc} would seem to be more likely.

In Fig. 11, we plot $(\chi_{loc})^{-1}$ versus T. The result is a Curie-Weiss curve with intercept (-32°K). The solid curve represents the perturbation theory result of Yosida and Okiji,[34] Scalapino,[35] and Giovannini, Paulson and Schrieffer.[37] These authors find that the susceptibility is given by

$$\chi=\frac{\mu^2}{3kT}\left[1+\frac{N(0)J}{1-N(0)J\ln(kT/D)}\right]. \quad (13)$$

This may be rewritten in terms of a "Kondo temperature"

$$kT_K=D\exp[1/N(0)J], \quad (J<0) \quad (14)$$

as

$$\chi=(\mu^2/3kT_K)\{[1-1/\ln(T/T_K)](T_K/T)\}. \quad (15)$$

For $7\leq T/T_K\leq 100$, the bracketed expression fits a Curie–Weiss type law to better than $\frac{1}{2}$% accuracy. Graphcial analysis shows that within these limits, Eqs. (13) or (15) may be rewritten

$$\chi=(\mu^2/1.22)/3k(T+4.5T_K), \quad (7\leq T/T_K\leq 100). \quad (16)$$

This expression has been normalized to the least-squares fit to χ_{loc} calculated for Fig. 7. This in turn determined the normalization of χ^{-1} to the data as presented in Fig. 11. Note that perturbation theory for χ^{-1} diverges for $T=eT_K=19.4$°K and strongly disagrees with the data for lower temperatures. On the other hand, there is good general agreement between theory and experiment for $T>40$°K. The remarkable aspect of the data is that χ_{loc}^{-1} is such a simple monotonic function of the temperature and shows no anomalous behavior at or below T_K.[38] The finite zero temperature result is in general agreement with predictions based on the many-body–singlet ground state.

In summary, the Mössbauer data together with the bulk-susceptibility measurements provides us with detailed information on the temperature dependence of χ as shown schematically in Fig. 12. The local susceptibility varies as $(T+32)^{-1}$ at all temperatures; whereas, at low temperature, $T<T_K$, an extra contribution to the total susceptibility builds which does not show up in the Fe^{57} hyperfine field and is therefore, presumably associated with a spatially extended spin density. The magnitude of this excess susceptibility is approximately equal to χ_{loc} for $T\ll T_K$. The solid curves in Fig. 12 represent actual data as described above while the dashed region in χ_{total} is drawn in such a way as to smoothly join the two curves for $T>T_K$ since reliable susceptibility data is not available in this transitional temperature range.[39]

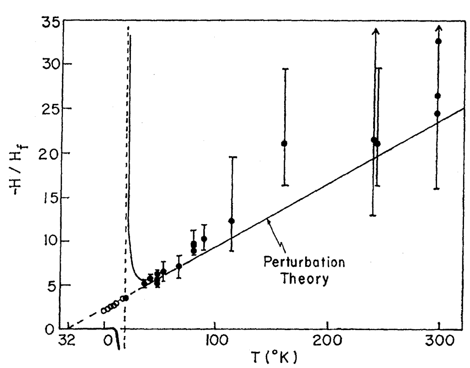

FIG. 11. The inverse local susceptibility χ_{loc}^{-1} as determined by the Mössbauer hyperfine measurements on dilute *Cu*Fe as a function of temperature. The solid curve represents the result of the perturbation-theory calculation of the inverse susceptibility.

[37] B. Giovannini, R. Paulson, and J. R. Schrieffer, Phys. Letters 23, 517 (1966).

[38] There are two reasons why the normalized theoretical expression for $1/\chi$ does not give the best "eyeball" fit to the data as presented in Fig. 11. First, as described above, the normalization was determined by the least-squares fit of Fig. 7. In that case, all data points [$-H_f$ versus $H/(T+32)$] had approximately the same statistical weight. On the other hand, a direct fit to the data in the form $H/-H_f$ versus T as presented in Fig. 11 must take into account the fact that the high-temperature points ($T>100$°K) have much smaller statistical weight than the low-temperature points. Second, in analyzing the data as presented in Fig. 7, we are able to take advantage of the fact that one must have $H_f\rightarrow 0$ as $T\rightarrow\infty$. In the plot of Fig. 11, this "data point" is of course indeterminate.

[39] The data of Hurd (see Ref. 33) do show an extra low-temperature susceptibility. However, he has indicated that his data below 17°K was experimentally unreliable (private communication).

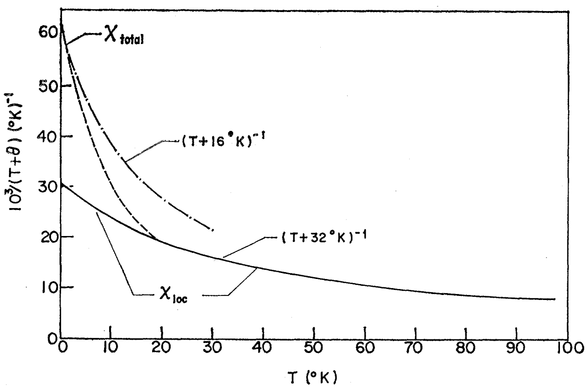

FIG. 12. Schematic diagram of the temperature dependence of the localized and total susceptibility per added Fe impurity in *Cu*Fe. The solid curves represent actual data as described in the text, whereas the dashed region in χ_{total} is drawn in such a way as to smoothly join the two curves for $T>T_K$ since reliable data is not available in the transitional temperature range.

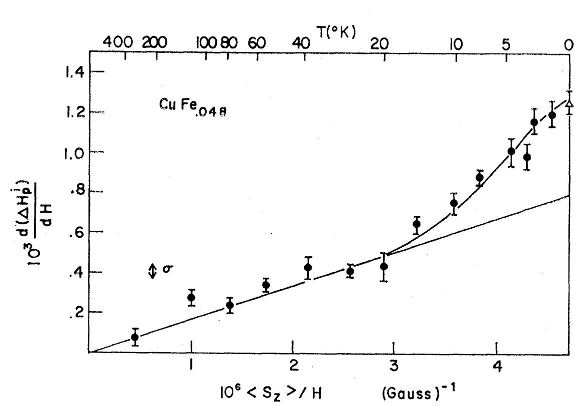

FIG. 13. The slope of the field dependence of the linewidth $d(\Delta H_p{}^i)/dH$ as a function of $\langle S_z{}^{Fe}\rangle/H$; i.e., versus the local susceptibility as obtained from the Mössbauer data. The solid line is a least-squares fit to the data for $T>20°K$ and represents the expected width if only RKKY spin-density oscillations were present. The extra contribution arises from the quasiparticle polarization.

IV. QUASIPARTICLE AMPLITUDE

The spin polarization around a partially polarized impurity as calculated from the Appelbaum-Kondo theory is given by

$$\sigma(r)=\sigma_0+\sigma_{RKKY}(r)+\sigma_Q(r). \quad (5)$$

The existence of the first two terms has been argued on very general grounds and verified experimentally in a large variety of systems. As given by Eqs. (6a) and (6b), $\sigma_{RKKY}(r)$ and $\sigma_Q(r)$ both have an explicit temperature and field dependence contained in $\langle S_z{}^{Fe}\rangle\sim H(T+32)^{-1}$ as well as an oscillatory spatial dependence. In the case of σ_{RKKY}, the coupling which determines the amplitude of the oscillations for given $\langle S_z{}^{Fe}\rangle$ will have no additional temperature or field dependence. By contrast, we expect the amplitude of σ_Q to have its full value only for $T=0°K$ and to be strongly reduced as T approaches T_K.[40] We also expect that the correlations which give rise to the quasiparticle will become ineffective upon application of sufficiently high magnetic fields. Our anticipation of such a field reduction of the quasiparticle is based on the work of Giovannini, Paulson, and Schrieffer[37] who show that for large enough fields, perturbation theory gives meaningful nondivergent results even for temperatures lower than T_K.

In Sec. III, we inferred, in a manner independent of any model, the existence of an extended polarization cloud by an analysis of the Mössbauer and bulk-susceptibility data. We now wish to obtain further information regarding the existence and properties of this nonperturbative spin density which we can denote phenomenologically as $\sigma_Q(r)$. Whatever the functional form of $\sigma_Q(r)$,[41] as long as it has a range greater than ~9 Å, we expect that it will contribute to the first, second, and higher moments of the total spin polarization and thereby affect the position and width of the NMR line. The minimum range requirement results from the fact that the amplitude of the RKKY oscillations are such that the host nuclei within a distance of about 9 Å from the impurity experience a Knight shift which is so large that they make no contribution to the observed line.[42] Thus, a $\sigma_Q(r)$ which affects only these nearest neighbors will have no effect on the resonance line.

In this section, we present a model-independent analysis of the nuclear-resonance experiments including both the data presented in Sec. II and the recently published data[12] for very low temperatures and fields up to 60 kG. The results demonstrate an extra contribution to the linewidth which builds up at low temperatures ($T<T_K$) and from which we obtain a measure of the temperature and magnetic-field dependence of the quasiparticle amplitude.

In Figs. 13 and 14, we plot the slopes $d(\Delta H_p{}^i)/dH$ and $d(\Delta H_{p2}{}^i)/dH$ versus $\langle S_z{}^{Fe}\rangle/H$; i.e., versus the local susceptibility as obtained from analysis of the Mössbauer data. If the RKKY term were the only contribution to the oscillating spin density, one would find a linear relationship between the NMR linewidth data and $\langle S_z{}^{Fe}\rangle/H$ [see Eq. (6a)]. Although the linear relationship appears to hold for $T\geq 20°K$, where perturbation theory should be valid, clearly evident in both figures is the approximately 50% additional contribu-

[40] J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).

[41] It is interesting to note that the spatial dependence given in Eq. (6b) is not unique to Kondo-Appelbaum theory. Fullenbaum has recently shown [thesis, University of Maryland, 1968 (unpublished)] that the ground-state spin-correlation function has the form $(\sin k_F r/r)^2$ in the original Nagaoka theory, in the Bloomfield-Hamann treatment of the Nagaoka theory, and in the Heeger-Jensen theory as well as in the Kondo-Appelbaum theory.

[42] Nuclei within a radius of about 2.5 lattice constants of a given impurity do not contribute to the observed NMR line. They are shifted far out into the wings by the large RKKY fields and therefore not observed. One can estimate the RKKY hyperfine field at a near-neighbor site as being of order 10^3 G.

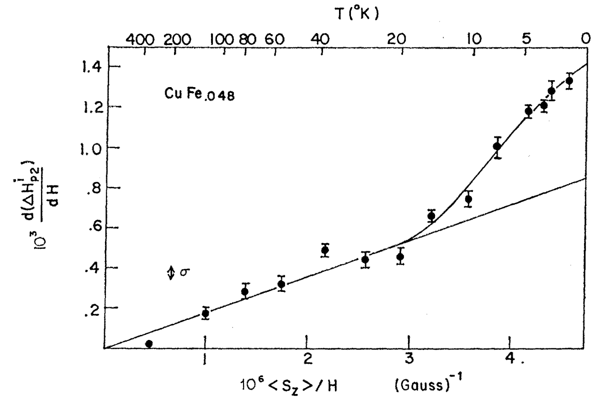

FIG. 14. The slope of the field dependence of the wing linewidth, $d(\Delta H^i{}_{p2})/dH$ versus $\langle S_z{}^{Fe}\rangle/H$. The results are in complete agreement with Fig. 13.

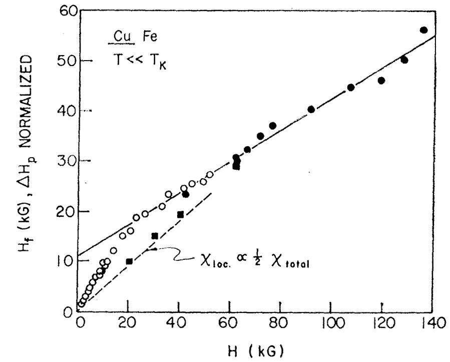

FIG. 16. Mössbauer hyperfine field and NMR linewidth (○) for *Cu*Fe versus magnetic field. The solid line represents a least-squares fit to the Mössbauer data for $H > 60$ kG. The NMR data have been normalized for continuity to the least-squares line at 50 kG. The "excess" linewidth at low fields arises from the quasiparticle spin polarization.

tion which develops as the temperature is lowered through T_K. We note, in addition, that the results shown in Figs. 13 and 14 are the same within experimental error indicating that even in the presence of the additional low-temperature correlations the field distribution $g_i(H)$ is Lorentzian. The straight lines on each figure were obtained by a least-squares fit of the data for $T \geq 20$°K.

We obtain a measure of the quasiparticle amplitude as a function of temperature by subtracting from $d(\Delta H_p{}^i)/dH$ and $d(\Delta H_{p2}{}^i)/dH$ the values which would be obtained if the broadening were due solely to the RKKY oscillations (i.e., the extrapolated straight lines of Figs. 13 and 14). These differences are then divided by $\langle S_z{}^{Fe}\rangle/H \propto (T+32)^{-1}$ to remove the explicit temperature dependence of the Fe local susceptibility and plotted in Fig. 15. Figure 15 thus represents the intrinsic temperature dependence of the quasiparticle amplitude, a quantity which provides perhaps the most fundamental description of the many-body spin correlations associated with the conduction electrons in the magnetic-impurity problem. The error bars represent our estimate based on the uncertainties in drawing the "best" curve through the $T < 20$°K data as well as possible error in the determination and extrapolation of the RKKY contribution for $T < 20$°K. As expected, the amplitude is strongly reduced as the temperature increases. However, there is no obvious "transition" temperature, and the curve appears to have a long high-temperature tail.

The dependence of the quasiparticle amplitude on magnetic field may be obtained in a similar manner from a comparison of the Mössbauer and NMR data. In Fig. 16, these data are shown for $T \ll T_K$. The Mössbauer data is the same as that of Fig. 8. The high-field NMR data is that of Ref. 12 with the extrapolated zero-field linewidth subtracted from each point. The two kinds of data have been normalized for continuity at the highest fields, where, as shown in Fig. 16, the slopes become the same. A simple proportionality is expected in the limit of large magnetic fields where the convergence of perturbation theory implies that only the RKKY contribution will remain. At smaller values of the magnetic field, the extra contribution to the linewidth is evident. Again we subtract the RKKY contribution (defined by the curve through the Mössbauer data), divide the difference by H to remove the explicit field dependence of the polarization, and plot the result as a function of the magnetic field in Fig. 17. Figure 17

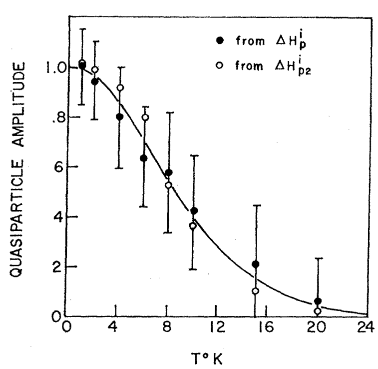

FIG. 15. The quasiparticle amplitude as a function of temperature as obtained from the NMR data. Note the long high-temperature tail.

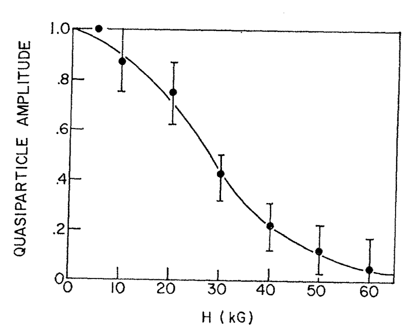

FIG. 17. The quasiparticle amplitude as a function of magnetic field as obtained from the NMR data.

thus represents the intrinsic dependence of the quasiparticle amplitude on the external field. The field and temperature dependence are virtually identical in functional form. However, the field dependence is more rapid by about a factor of 3 than would be obtained from Fig. 15 by simply converting according to the relation $g\mu_B H = kT$ with a g value of 2. On the other hand, the work of Giovannini *et al.*[37] shows that for spin $\frac{1}{2}$, perturbation theory breaks down (for very low temperatures) at $2\mu_B H_c = kT_K$. Using $T_K = 7.1$°K, as obtained from Eq. (16) and the high-temperature susceptibility data, one finds $H_c \simeq 53$ kG in good agreement with the magnitude of field needed to effectively destroy the quasiparticle as seen in Fig. 17. It appears, however, that *temperatures* of order $3T_K$ are needed to knock down the quasiparticle correlations to the same extent.

V. VERY-LOW-FIELD DATA

We now turn to a discussion of the very-low-field behavior of the NMR experiments. Referring again to the data presented in Figs. 3 and 4 we note that the linewidths extrapolated to zero field are somewhat higher than the values of $\Delta H_p = 6.4$ G and $\Delta H_2 = 11$ G appropriate for pure Cu. Alternatively one may say that the impurity contribution to the linewidth (Figs. 5 and 6) does not extrapolate to zero in zero field. In Fig. 18, we present the values of the zero-field intercept obtained from the least-squares analysis of the data. Although there is considerable scatter, the over-all feature of this data is that there is a gradual increase of $\Delta H_p^i | H = 0$ with decreasing temperature which saturates below 1°K. In the low-temperature $T = 0.03$–0.3°K region, a temperature-independent intercept was found which increased with impurity concentration, somewhat faster than linearly.

In the present work, the 1.2°K linewidth measurements were extended down to magnetic fields as low as 170 G. As can be seen in Fig. 19, ΔH_p and ΔH_2 rapidly approach the pure Cu values below 2 kG. In Fig. 20, we present ΔH_p^i and ΔH_{p2}^i for these data, and again we note that the impurity contribution to the linewidths tend to zero below 3 kG. [Note that the agreement between the values of ΔH_p^i and ΔH_{p2}^i supports the assumption of a Lorentzian $g_i(H)$ over the entire range of magnetic fields.] Thus we see that the origin of the zero-field intercept is a field-dependent NMR susceptibility which has a high initial value and rapidly decreases to a constant value for fields greater than 3 kG.

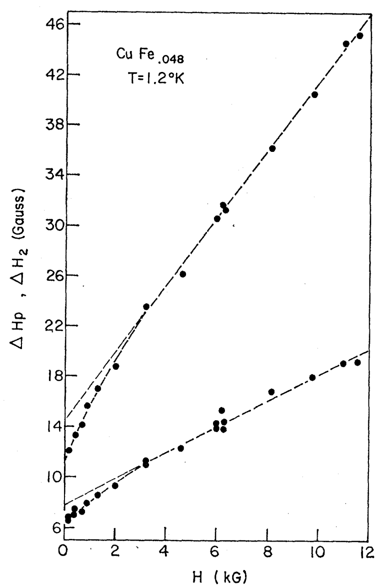

FIG. 19. Complete field dependence of ΔH_p and ΔH_2 for Cu^{63} in CuFe$_{0.048}$ at 1.2°K. The measurements extend from 170 to 12 kG. Note the rapid approach to the pure Cu values at fields below 2 kG.

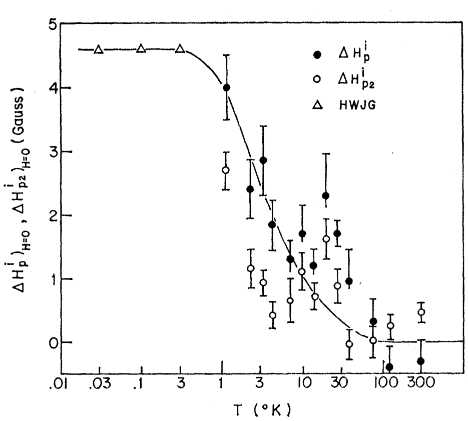

FIG. 18. The extrapolated zero-field linewidth intercept versus temperature.

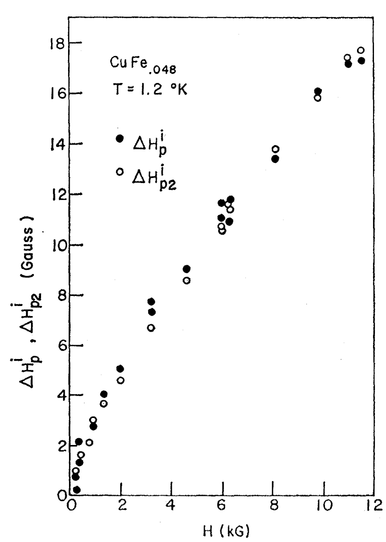

FIG. 20. ΔH_p^i and ΔH_{p2}^i as a function of field. The anomalous field dependence at low fields (<2 kG) is noted. The agreement between ΔH_p^i and ΔH_{p2}^i implies a Lorentzian local-field distribution over the entire field range.

Similar behavior has been observed in bulk-susceptibility measurements of *Cu*Fe by Daybell and Steyert.[32] They found a low-temperature ($T \ll 1°K$) susceptibility which for zero field had a $T^{-1/2}$ temperature dependence and which saturated above 1 kG to a temperature-independent value equal to $\mu_{\text{eff}}^2/3kT_K$. As they point out, this weak temperature dependence agrees with a preliminary calculation of Anderson[43] although it has not been possible to account for the saturation in fields as low as 1 kG within the Anderson theory. Moreover, other calculations[12,44] of the low-temperature susceptibility do not yield such a term. The similarity of the NMR linewidth and bulk-susceptibility measurements strongly suggest that these low-field data are of the same origin.

We wish to point out an alternative explanation of this low-field susceptibility based on the phenomenon of superparamagnetism.[45] Such an explanation provides a good qualitative understanding of the low-field behavior of both the NMR and bulk-susceptibility data. Consider an ensemble of very small single-domain ferromagnetic particles such as would be obtained if a fraction of the Fe impurities were to precipitate out of solution. Provided the thermal relaxation to the surrounding host is short enough compared to experimental times, then the magnetization of the ensemble will be given by the classical Langevin function

$$\bar{\mu} = \mu[\coth(\mu H/kT) - (kT/\mu H)], \qquad (17)$$

where μ is the total moment of an individual particle. [One should go one step further and consider a statistical average of Eq. (17) due to the distribution of particle sizes. However, this kind of precision is not called for in the qualitative arguments presented here.] Such a system will have a large initial susceptibility and will saturate in a relatively small magnetic field because of the large moments of the particles. Moreover, a nonlinear dependence on concentration of Fe would be expected. This type of behavior has been observed in relevant systems such as Fe in Cu,[46] Fe in β brass,[47] and Co in Cu.[48] Of course, in the studies of superparamagnetism, precipitation was purposely encouraged by starting with an impurity concentration in the range 0.1–2 at.% and annealing at intermediate temperature. On the other hand, the alloys for the experiments we are concerned with were prepared so as to preserve a true solid solution. The generally accepted procedure is to work with very dilute alloys and rapidly quench the samples from an anneal at a temperature high enough

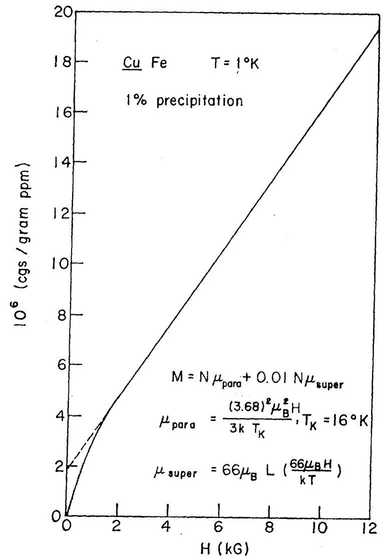

FIG. 21. M versus H for *Cu*Fe in which 1.0% of the Fe atoms have precipitated in small superparamagnetic clusters of 30 Fe atoms each (see text).

that the solubility is large. Despite these best efforts, let us consider the effect of a small amount of precipitation. Suppose for example that a small fraction of the impurity atoms were to form clusters of 30 Fe atoms each. This corresponds to a spherical particle with a 4.5 Å radius. For bulk ferromagnetic Fe, each atom has an average moment of 2.2 μ_B so that one would expect that the proposed clusters would have a moment of 66 μ_B. We show in Fig. 21 the form of M versus H for such a system based on these assumptions and calculated for 1% precipitation and 1°K. The results are remarkably similar to the linewidth data of Fig. 20. In addition, for the same particle size, only 0.1% precipitation would give a susceptibility at 0.2°K of about 0.15 emu/g ppm in rough agreement with the magnitude of the initial χ found by Daybell and Steyert.[32]

The temperature dependence in such a model is complicated by relaxation effects. The thermal relaxation time to the surrounding host is given by[45]

$$1/\tau = f_0 \exp(-KV/kT), \qquad (18)$$

where f_0 is a characteristic frequency of the order of 10^9 sec^{-1}, K is the anisotropy constant, and V is the volume of the particle. For a K of 6×10^5 erg/cm^3, a particle volume of 3.5×10^{-22} cm^3, and a temperature of 1°K, one finds a τ on the order of nanoseconds. However, the strong exponential behavior of Eq. (18) causes τ to increase rapidly to a value of hours at 50 mdeg. Consequently one could not expect an ac susceptibility experiment, such as used by Daybell and Steyert, to observe the ideal Langevin behavior over the entire temperature range. The result of such a measurement would be a temperature dependence less rapid than $1/T$. However, the exact form is difficult to calculate and

[43] P. W. Anderson, Phys. Rev. **164**, 352 (1967).

[44] H. Ishii and K. Yosida, Progr. Theoret. Phys. (Kyoto) **38**, 61 (1967).

[45] For a general discussion see I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by H. Suhl and G. Rado (Academic Press Inc., New York, 1963), Vol. III, Chap. 6.

[46] F. Bitter, A. Kaufman, C. Starr, and S. T. Pan, Phys. Rev. **60**, 134 (1941).

[47] A. E. Berkowitz and P. J. Flanders, J. Appl. Phys. Suppl. **30**, 111S (1959).

[48] J. J. Becker, Trans. AIME **209**, 59 (1957).

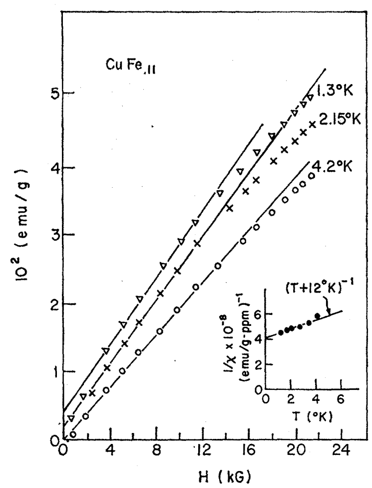

FIG. 22. Magnetization data of Hedgcock, Muir, Raudorf, and Szmidt (see Ref. 49).

depends in a very sensitive way on the particle-size distribution.

The above numbers are admittedly crude guesses and cannot be taken literally. They do, however, make an explanation of the low-field behavior based on a superparamagnetic mechanism highly plausible. It is difficult to think of a way of conclusively settling this point experimentally. The precipitated Fe is evidently in such small quantities that even Mössbauer studies would not see them.

There is one further source of information on the magnetic properties of the *Cu*Fe systems available in the form of magnetoresistivity experiments.[49,50] Unfortunately the interpretation of the spin-dependent component of the magnetoresistance is not completely straightforward. However, the data published by Hedgcock *et al.*[49] is presented in such a manner that one can read off a direct measurement of magnetization versus field and thus avoid the interpretational difficulties. These data for three temperatures are shown in Fig. 22. The straight lines were drawn to fit the data between 3 and 12 kG as in the NMR case. Although the concentration of Fe was a relatively large 0.11 at.%, the general features of the data are very consistent with the NMR and bulk-susceptibility data already discussed. The susceptibility obtained from the slope of the fitted line obeys a $(T+12)^{-1}$ law. This is shown in the insert of Fig. 22 and further confirms the increase of χ_{total} at low temperatures. Below 3 kG, the susceptibility is considerably larger. This initial susceptibility increases as the temperature is lowered. We see that the effect of this initial rapid increase in the magnetization is to make the linear intermediate-field data appear to have a nonzero intercept. Once more, this is just the behavior one could expect from a small precipitation of superparamagnetic particles. On the other hand, once again Hedgcock *et al.* point out that the initial susceptibility also agrees well with the $T^{-1/2}$ law. Finally, we note the deviation of M from linearity for fields above 14 kG. This behavior compares favorably with the nonlinear behavior beginning at 16 kG for the NMR data (Fig. 16).

VI. CONCLUSION

In an attempt to verify the existence of the extended spin-polarization cloud associated with the ground state of the magnetic impurity problem, we have presented results of a new comprehensive set of NMR measurements together with a review of all the available "susceptibility" data (i.e., bulk susceptibility, Mössbauer, and NMR) on *Cu*Fe.

The results demonstrate the existence of the quasiparticle polarization cloud in this system. By a model-independent analysis of the data, we obtain a measure of the temperature and field dependence of these low-temperature spin correlations. Although the results are in qualitative agreement with the Appelbaum-Kondo many-body singlet, which provided a theoretical guide and motivation, detailed comparison of experiment with this or any theoretical treatment requires a calculation of the second and fourth moments of the spin density as worked out within that particular model and comparison of such calculations with the experimentally determined moments of the NMR line. Such a study is in progress for the Appelbaum-Kondo theory and will be published elsewhere.[51] We emphasize, however, that in this paper, the existence of the quasiparticle polarization and the temperature and magnetic field dependence of the amplitude are inferred by means independent of any model.

The temperature-magnetic field boundary defining the region of the H-T plane over which the quasiparticle amplitude is sizable agrees qualitatively with the boundary defined by the breakdown of perturbation theory. There are three points of particular interest in this regard. First, there is no real boundary. Both Figs. 15 and 17 show long tails which probably only approach zero asymptotically. The quasiparticle amplitude $\sigma_Q(r)$ is perhaps analogous to the order parameter in superconductivity in that it is a measure of the many-body correlations in the conduction-electron system. In the superconductivity case, the order parameter approaches zero with infinite slope as $T\rightarrow T_c$. This is clearly not the case here. The difference is related to the very small number of degrees of freedom associated with the condensed state of the impurity problem. As a result, it seems evident that a treatment of the temperature and field dependence from the point of view of noninteracting elementary excitations from a singlet ground state will be valid only in the very-low temperature low-field limit. Forturnately, other more sophisticated tech-

[49] F. T. Hedgcock, W. B. Muir, T. Raudorf, and R. Szmidt, Phys. Rev. Letters **26**, 457 (1968).
[50] P. Monod, Phys. Rev. Letters **26A**, 581 (1968).
[51] D. Golibersuch and A. J. Heeger (to be published).

niques are evolving[52] which may be able to eventually bridge the transitional region.

The second point is the interesting result that although the field and temperature dependence of the quasiparticle amplitude are experimentally of the same form, a temperature of order $3T_K$ is needed to effectively destroy the quasiparticle whereas a field such that $g\mu_B H_c = kT_K$ is sufficient. Although the difference may be simply a matter of proper definitions, this does not seem to be the case if one defines T_K as that temperature below which a perturbative calculation of the susceptibility or the resistivity diverges. This brings us to the third point; namely, why indeed does the quasiparticle break up with increasing magnetic field? One knows that this must be the case because of the high-field perturbative limit. Nevertheless, since the existence of the quasiparticle seems to double the total susceptibility contributed per impurity, the breakup of these spin correlations would appear to cost energy! Evidently the answer is more subtle. The ground-state spin correlations in the conduction-electron system may be viewed as arising from an indirect electron-electron interaction via the intermediate impurity spin. The effect of an external field is to alter the energy denominators in the intermediate states of this indirect interaction (in a field H, an energy $g\mu_B H$ is required to flip the impurity spin). Thus the field acts in such a way as to alter the basic interaction which leads to the conduction-electron spin correlations. Finite temperature might well then be expected to have a smaller effect since the dominant low-temperature excitations are not impurity spin flips but electron-holelike excitations in the electron gas. Such arguments are plausible, if not convincing, and seem worthy of further study.

We have proposed an explanation of the anomalous low-field susceptibility based on superparamagnetism of small clusters of precipitated Fe atoms. The strongest arguments in favor of such a mechanism are the low saturation field ($\sim$2 kG) even at temperatures above 1°K, and the fact that the *Cu*Fe system is a known example of such effects. However, the temperature dependence is difficult to pin down. One can only say it should be less rapid than T^{-1}. Because of the very minute amount of precipitated Fe needed to explain the data, it will be difficult to obtain direct evidence of such clusters.

Finally, one might ask if the singlet-ground state concept is truly fundamental to the low-temperature properties of the impurity–conduction-electron system. The answer appears to be both yes and no. On the one hand, the singlet idea offers a natural explanation for the extended quasiparticle spin correlations. However, Fig. 16 shows that the local susceptibility is changed only slightly with fields that are sufficient to essentially destroy the quasiparticle. In addition, the local susceptibility is almost insensitive to the build up of the quasiparticle with decreasing temperature (Fig. 10). It seems that there are two aspects of the problem which can be more or less separated; the local susceptibility and the quasiparticle spin-polarization cloud. The fact that such a separation is possible reconfirms the often stated argument that true local-moment behavior requires a small conduction-electron–local-orbital-mixing matrix element. Of course such a complete division of electronic effects is an oversimplification. The two spin systems certainly are interdependent. Thus, we emphasize that as the quasiparticle builds up with decreasing temperature there is an observable increase in the local susceptibility (Fig. 10). As the quasiparticle amplitude is reduced by an increasing magnetic field ($T \ll T_K$), one does see a decrease in $\chi_{\rm loc}$ (Fig. 16). This apparent renormalization of the local moment caused by the presence of long-range conduction-electron correlations is not accounted for by present theories.

This hint of a renormalization of the impurity spin suggests an alternative explanation of the data. It is possible that the positive-definite part of the spin density resides in a very small region of space within a few lattice constants of the impurity and that a self-consistent treatment of the conduction-electron scattering from such a relatively localized "giant" moment will lead to an ehnanced amplitude of the RKKY oscillations. In other words, a spatial spin distribution roughly similar to that appropriate for dilute Pd alloys (e.g., *Pd*Fe and *Pd*Co) would be consistent with the data. We note in this respect that the one parameter not determined in the present analysis is the range of the quasiparticle cloud. From the NMR linewidth data, one can infer only that the conduction-electron spin polarization is enhanced at distances greater than 9 Å [42] for temperatures below T_K. Information on the range of the positive-definite spin polarization is contained in the first moment or shift of the NMR line. Such a shift has been observed.[15] However, the shift is a small effect in *Cu*Fe [53] and not completely convincing so that this question remains open.

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[52] P. E. Bloomfield and D. R. Hamann, Phys. Rev. **164**, 856 (1967); H. Suhl, *ibid.* **138**, 515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966); A. A. Abrikosov, Physics **2**, 5 (1965). Unfortunately, these theories which are so far based on the Nagoaka truncation [Y. Nagaoka, Phys. Rev. **138**, A1112 (1965)], or an equivalent approximation, are not correct in the low-temperature limit [Zittartz (private communication)]. However, they do make contact with perturbation theory in the high-temperature limit and remove the divergence in a self-consistent manner.

[53] The larger shifts which were analyzed in Ref. 12 for the AuV system are of a different origin as shown by recent NMR studies [A. Narath (private communication)].