Ground State of the Magnetic Impurity Problem; Nuclear-Magnetic-Resonance Studies of Dilute Copper Alloys*

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We report here nuclear-magnetic-resonance (NMR) studies of dilute alloys of Cu containing *3d* transition-element impurities at temperatures above 0.03°K. The impurity contribution ΔH to the Cu^{63} NMR linewidth was measured in applied magnetic fields up to 50 kOe for *Cu*Fe and up to 11 kOe for *Cu*Cr, *Cu*Mn, and *Cu*Co. The *Cu*Fe and *Cu*Cr alloys exhibit several remarkable features. First, ΔH is greatly reduced from the value expected from high-temperature linewidth measurements. Second, ΔH is linear in concentration and in field, but independent of temperature at low temperature. Thus ΔH does not follow a free-spin Brillouin function, but is well fitted by $\Delta H/H$ proportional to $(T+T_K)^{-1}$, where $T_K=14$°K for *Cu*Fe and $T_K=1.4$°K for *Cu*Cr. Both values agree with Kondo temperatures obtained by other methods. Third, ΔH is found to be proportional to previously published susceptibility data for *Cu*Fe alloys, indicating the persistence of Ruderman-Kittel-Kasuya-Yosida (RKKY) spin-density oscillations with magnitude proportional to $\langle S_z\rangle$ even for $T\ll T_K$. No evidence is seen for either a $\ln T$ or a $T^{-1/2}$ contribution to ΔH. The field dependence of $\Delta H(T\ll T_K)$ for *Cu*Fe and *Cu*Cr alloys changes slope at applied fields of 25 and 2.5 kOe, respectively, in disagreement with the calculation of Nam and Woo. The slope change is a factor of 2.5 for *Cu*Fe and 5 for *Cu*Cr. The effects of short-range order upon ΔH were studied in a 200-ppm *Cu*Mn alloy below the "ordering" temperature. The data show a large field-independent linewidth and are consistent with a saturation of the impurity spins along their local axis of quantization. We conclude that short-range magnetic order cannot lead to the effects seen in *Cu*Fe and *Cu*Cr. The field dependence of *Cu*Co is consistent with $T_K>1000$°K. An equation-of-motion calculation of the initial susceptibility χ and the spin polarization about the impurity, $\sigma(r)$, is presented. The theory is based upon the Kondo-Applebaum many-body singlet ground state of the magnetic impurity problem. For the static susceptibility, we find

$$\chi=\chi_{\text{Pauli}}+2g^2\mu_B^2/[\tfrac{4}{3}\ln(D/kT_K)]kT_K,$$

and for the spin polarization near the impurity

$$\langle\sigma(r)\rangle=\langle S^z\rangle[A(\cos 2k_Fr)/(k_Fr)^3+B((\sin k_Fr)/k_Fr)^2].$$

The first term is the well-known RKKY spin-density oscillation. The second term arises from the polarization of the quasiparticle in an external field. Whereas the first term accounts for the field-dependent linewidths of *Cu*Fe and *Cu*Cr, the second term is negative definite, giving rise to an excess Knight shift. The excess Knight shifts for the Cu alloys and for V^{51} in *Au*V (0 to 10%) are calculated and found to be in reasonable agreement with experiment. This agreement supports the existence of the extended range of the quasiparticle polarization, and provides the first indirect measurement of the coherence length for the magnetic impurity problem.

I. INTRODUCTION

THE properties of dilute alloys of transition-element impurities in nonmagnetic metals have been the subject of considerable attention in recent years. In particular, as a result of Kondo's explanation[1] of the well-known resistance minimum phenomenon in metals containing magnetic impurities there has been renewed interest in the problem. Perturbation-theory calculations of physical quantities using an isotropic *s-d* exchange Hamiltonian ($H=J\mathbf{S}\cdot\mathbf{s}$) to treat the interactions between the conduction-electron spins ($\mathbf{s}$) and the impurity spin ($\mathbf{S}$) give results of the form

$$\Delta\rho=c\rho_m[1+N(0)J\ln(kT/D)+\cdots] \quad (1)$$

for the magnetic contribution to the resistivity, where c is the impurity concentration, ρ_m is the Born scattering term, J is the *s-d* exchange coupling constant, and $N(0)$ is the density of states in a flat band of width $2D$. Similarly,[2,3]

$$\langle S_z\rangle=(g\mu_BH/kT)\times[1+N(0)J(1+N(0)J\ln(kT/D)+\cdots)] \quad (2)$$

for the impurity spin polarization in an external field H. One sees in each case a logarithmic divergence which indicates a breakdown of perturbation theory at temperatures below the characteristic Kondo temperature

$$kT_K\cong De^{-N/N(0)J}. \quad (3)$$

However, the appearance of a divergence in perturba-

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† National Science Foundation Predoctoral Fellow.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

[2] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 504 (1965).

[3] D. J. Scalapino, Phys. Rev. Letters **16**, 937 (1966).

tion theory is clearly not a solution of the problem as much as it is a demonstration of the need for further study, both theoretical and experimental, of the low-temperature properties of such a system.

The logarithmic divergence appearing in the perturbative calculations arises from the Fermi factors which characterize the distribution of the electrons in the Fermi sea. The fact that, for example, the electron scattering off the impurity is sensitive to the distribution of the *other* electrons is an indication that this is a true many-body problem. Physically, a conduction electron scatters from the impurity, flipping the impurity spin so that the scattering of a second conduction electron depends on the previous history of scattering events.[4] In other words, there is an effective many-body electron-electron interaction (via the impurity) intrinsic to the magnetic impurity problem, which is reminiscent of the effective electron-electron interaction (via virtual phonons) which can lead to superconductivity. Thus one cannot separate the N-electron problem of an electron gas with a magnetic impurity into N one-electron scattering problems.[5] The problem is, therefore, one of understanding the nature of the ground state of this many-body system.

The theoretical question of whether or not one is to expect a many-body condensed state has been the subject of some controversy. However, variational treatments of the problem[6–8] using singlet or triplet many-body wave functions as well as self-consistent Green's-function techniques[9,10] have demonstrated the existence of coherent states with a nonanalytic binding energy [similar to the expression for kT_K given in Eq. (3)] relative to the perturbative treatments of the problem. Such results do not imply a sharp phase transition from one state to another,[4] for such a cooperative effect is impossible in a system with a small number of degrees of freedom. Rather, one expects a gradual breakup of the spin correlation with increasing temperature.

That there is a nondegenerate many-body condensed state for the magnetic impurity problem is suggested by a variety of experimental studies of such properties as low-temperature electrical resistivity, electronic specific heat, and magnetic susceptibility, together with a more microscopic view provided by NMR[11] and Mössbauer effect.[12] Extension of the resistivity measurements to temperatures below T_K shows an eventual saturation at a value consistent with the unitarity limit for d-wave scattering (maximum phase shift $\frac{1}{2}\pi$). The lack of subsequent decrease in the resistivity far below T_K would seem to rule out a simple scattering resonance[13] or the onset of magnetic order as sources for the anomalous behavior. In fact, the linear concentration dependence of all low-concentration properties indicate these properties result from the behavior of isolated impurities in the metal. The susceptibility in a variety of systems[14–17] has been fit with a form (see Sec. IV)

$$\chi \propto (T+\theta)^{-1}, \tag{4}$$

where θ is independent of concentration for low concentrations. Perhaps the most revealing of the macroscopic measurements is the low-temperature specific heat, particularly the work of Frank, Manchester, and Martin[18] on the *Cu*Fe system. These results show a low-temperature anomaly with a maximum at a temperature which is independent of concentration. Moreover, the integrated area under these curves is consistent with the removal of the magnetic entropy of the impurity spins. Thus the presence of a nondegenerate many-body condensed state for the magnetic impurity problem is consistent with the experiments. The remaining uncertainty is simply the very unlikely possibility that clustering, inhomogeneity, or some kind of bizarre ordering of the impurities could lead to the observed experimental results. One can, however, convincingly rule out these latter possibilities by microscopic experiments, e.g., by the NMR studies reported here.

The technique of NMR is well suited for studies of dilute alloys, for those nuclei in the vicinity of a given impurity atom are sensitive to the local conduction-electron spin polarization. This spin polarization is set up whenever a magnetic impurity is introduced into a nonmagnetic metallic host, since the conduction electrons scatter from the spin-dependent impurity potential. The resulting spin-density oscillations are a direct consequence of the Fourier transformation of the sharpness of the Fermi surface in k space. Although no low-temperature behavior of the system can change this sharpness on scales greater than $k_F(kT/E_F)$, the size and spatial form of the oscillations could be

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[8] J. Kondo, Progr. Theoret. Phys. (Kyoto) **36,** 429 (1966); J. Applebaum and J. Kondo, Phys. Rev. Letters **19,** 906 (1967); and Phys. Rev. **170,** 542 (1968).
[9] Y. Nagaoka, Phys. Rev. **138,** A1112 (1965); Progr. Theoret. Phys. (Kyoto) **37,** 13 (1965).
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[13] G. J. van den Berg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. IV.
[14] M. Daybell and W. Steyert, Phys. Rev. **167,** 536 (1968).
[15] G. Knapp, J. Appl. Phys. **38,** 1268 (1967).
[16] C. M. Hurd, Phys. Rev. Letters **18,** 1127 (1967).
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affected by the low-temperature behavior. The conventional perturbative calculation gives the familiar RKKY[19] spin density of the form

$$\sigma(r)\sim(\cos 2k_F r)/r^3.$$

However, we have seen that at sufficiently low temperatures a perturbative treatment of the conduction-electron–impurity interaction breaks down. Thus one does not know *a priori* either the magnitude or the spatial depencence of the conduction-electron spin polarization for $T<T_K$. Suhl[20] has demonstrated the persistence of spin oscillations of the RKKY form even at low temperatures, but without being able to include the effect of spin correlations on the Curie constant or the conduction-electron polarization (see Sec. IV).

The resulting spin oscillations can be probed by the nuclear spins of the host metal via the hyperfine interaction

$$\mathcal{H}=A_N\mathbf{I}\cdot\mathbf{s},$$

where A_N is the hyperfine coupling constant and $\mathbf{I}$ is the nuclear spin. The nuclear resonance on the host nuclei therefore gives information on the nature of the *magnetic properties* of the ground state.

We present here NMR data on dilute alloys of Mn, Fe, Cr, and Co in Cu metal. Because of the small value of T_K for *Cu*Mn,[21] the internal exchange fields due to indirect Mn–Mn interactions would be expected to self-quench the Kondo effect in this system at the concentrations, fields, and temperatures studied. The *Cu*Mn NMR results indicate non-spin-compensated behavior and are consistent with the known existence of short-range magnetic order for the Mn spins.[22] The data on the Fe and Cr alloys, on the other hand, are qualitatively different and indicate singletlike nonmagnetic ground states with characteristic Kondo temperatures T_K of about 14°K for *Cu*Fe and 1.4°K for *Cu*Cr. The data for the Fe and Cr systems are similar when suitably scaled to the value of T_K.

The apparatus and experimental techniques are described in Sec. II. The NMR data on the temperature and field dependence of the linewidth for the Mn, Fe, Cr, and Co systems are described and compared in Sec. III; and a theory is developed for the susceptibility and spin polarization for a Kondo-Applebaum many-body singlet in Sec. IV. In Sec. V we compare the results with theory and attempt to summarize the current experimental and theoretical situation.

II. SAMPLES AND APPARATUS

In this paper we report measurements made on a series of dilute copper alloys containing the following concentrations of $3d$ transition elements: 0.018, 0.041, 0.061, and 0.071 at.% Fe, 0.02 at.% Mn, 0.0047 at.% Cr, and 0.04 at.% Co. Some of the alloys were prepared in our laboratory and some were purchased from Materials Research Corporation in Orangeburg, N. Y. Those samples prepared in our laboratory were arc-melted in an argon-arc furnace from 99.999% pure Cu purchased from the American Smelting and Refining Co. The analysis of the starting material lists less than 3 ppm of transition-metal impurities. As discussed below (Sec. III) the alloys obtained from MRC contained less than 5 ppm of magnetic impurities other than the desired one. After arc-melting the alloys were annealed at 800 to 900°K for 2 or 3 days followed by quenching into water. In all cases, the solubility limit of the impurity in copper at the annealing temperature was at least an order of magnitude above the actual concentration. Metallographic examinations made on the most concentrated alloys showed no indication of precipitation or cluster formation on the grain boundaries.

The resistivity ratio was measured to within 10% for the *Cu*Fe alloys, yielding impurity concentrations in agreement with chemical analyses to within 20% In fact, the resistivity measurement is probably the most reliable way of determining the actual concentra

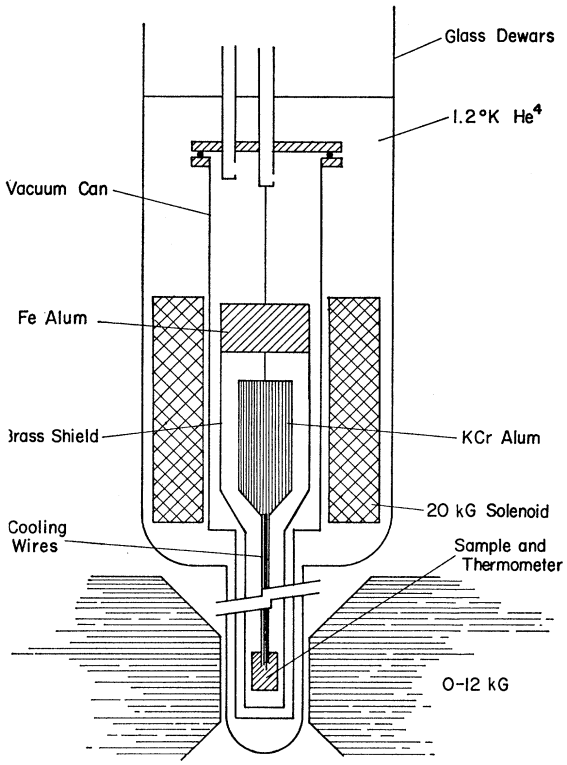

FIG. 1. Demagnetization apparatus (not to scale) showing the 20-kG superconducting solenoid used for demagnetizing KCr alum and Fe alum. The sample is connected to the cooling salt by Cu and then Ag wires.

[19] For a discussion, see C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1961), p. 360.
[20] H. Suhl, Solid State Commun. **4**, 487 (1966).
[21] I. A. Campbell, J. P. Compton, I. R. Williams, and G. V. H. Wilson, Phys. Rev. Letters **19**, 1319 (1967).
[22] S. D. Silverstein, Phys. Rev. Letters **16**, 466 (1966).

tion of impurities in solution since it measures the actual number of impurities which scatter the conduction electrons. Thus impurities which have been effectively removed from the alloy due to clustering on grain boundaries or internal oxidation are not included in the resistivity. Resistivity data[23] on alloys containing from 22 to 560 ppm Fe show a linear concentration dependence indicating that such alloys can be prepared free from clustering or other metallurgical problems. As an additional check we measured the resistivity ratio on some samples both before and after the homogenizing anneal and found no variations within the 10% experimental error.

Almost all the data reported here were obtained using a two-salt adiabatic demagnetization apparatus as shown schematically in Fig. 1. Both salts were suspended by nylon threads within the core of a 20-kOe superconducting magnet. The upper salt (Fe alum) was connected to a brass shield surrounding both the lower salt (Cr alum) and the sample so that the Fe alum served as a thermal shield between the Cr alum and the liquid He^4 bath. Both salts were crystalized from supersaturated soutions about Cu wires which provided the thermal contact. The sample was suspended about 20 in. below the Cr alum in order to avoid interactions between the superconducting magnet and the Varian electromagnet which supplied the magnetic fields for NMR. Thermal contact between the paramagnetic salts and the He^4 bath was established with 1 mm of He^4 gas. After the salts had been magnetized and thermal equilibrium established at 1.2°K, the He^4 gas was pumped out. When the paramagnetic salts were demagnetized, residual He^4 gas was adsorbed by the Cr alum. Run times of several hours were obtained in this manner for temperatures below 0.1°K.

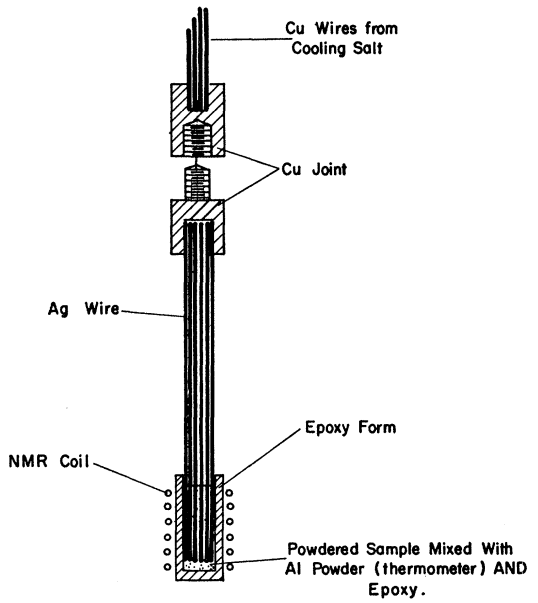

FIG. 2. Sample container and NMR coil. Epoxy is used to thermally connect the sample (e.g., *Cu*Fe) powder, Al powder (NMR thermometer), and Ag wires coming down from the cooling salt. The NMR coil is wound directly around the epoxy form.

[23] M. Daybell and W. Steyert, Phys. Rev. Letters **18**, 398 (1967).

The construction of the sample pill is shown schematically in Fig. 2. Particles of the alloy in question were obtained by filing by hand or with a converted mechanical hacksaw. After the particles were passed through a strong inhomogeneous magnetic field in order to eliminate any magnetic inclusions, they were mixed with epoxy in a cylindrical mold 1 cm long and 5 mm in diameter. Roughly a hundred 0.005-in. Ag wires were set into the epoxy to provide thermal contact between the alloy particles and the Cr alum. A 10–20-turn NMR coil was wound around the sample pill and fixed in place with *Q* dope. The resonance data were obtained using a low-level Robinson oscillator modified for frequency modulation. In order to prevent sample heating and to avoid saturation effects in the nuclear spin system at the lowest temperature, rf levels were kept lower than 30 mV. At higher rf levels heating effects could be observed. The output of the Robinson oscillator was amplified with a phase-sensitive lock-in amplifier and displayed on a chart recorder.

Temperature measurements were made from 1 to 4°K using calibrated 100-Ω Allen-Bradley carbon resistors and from 0.02 to 1.0°K using calibrated 220-Ω Speer carbon resistors. The enamel coatings of both types of resistors were ground off to provide better thermal contact to the sample. The Allen-Bradley resistors were calibrated, using He^4 vapor-pressure data. The Speer resistors were calibrated to within 5% from the Curie-law temperature dependence of the amplitude of the Al NMR signal from a sample containing Al powder while taking care that the rf level, modulation amplitude, etc., were constant throughout the calibration. The temperature calibrations were made with sample pills constructed in the same way as the sample pill containing the alloy, thereby eliminating questions that arise concerning poor thermal contacts or thermal gradients. Temperature checks were also made on some samples by mixing a small amount of Al powder directly in with the alloy particles. This was not normally done as the Al^{27} and Cu^{63} NMR signals overlap somewhat in low fields. The Curie-law nuclear spin susceptibility provides an excellent temperature scale in this range and can readily determine temperatures with a few percent accuracy.

III. EXPERIMENTAL RESULTS

In 1959 Sugawara[24] reported a comprehensive experimental investigation of the NMR in Cu alloys containing 3*d* impurities. The present work extends that investigation to lower temperatures in order to study the ground state. Sugawara found that the NMR

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

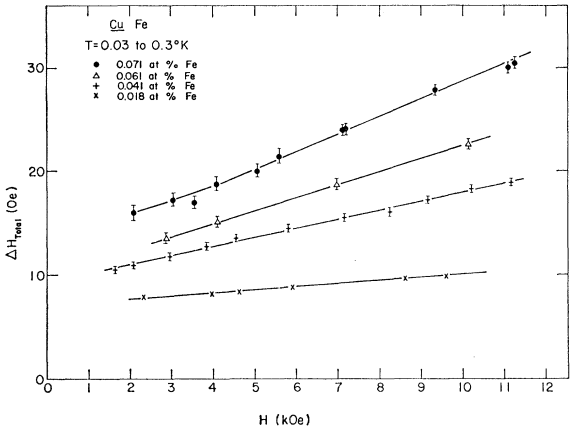

FIG. 3. Total (*peak-to-peak*) linewidth as a function of field for *Cu*Fe samples of four different concentrations (0.018, 0.041, 0.061, and 0.071 at. % Fe). The data are independent of temperature in the range 0.03 to 0.3°K.

line shape was inhomogeneously broadened in such random alloys and that the impurity contribution to the line shape was Lorentzian. In this case the total line shape $I(H)$ of the NMR line is given by

$$I(H)=\int_{-\infty}^{+\infty} g(H-H')l(H')dH', \qquad (5)$$

where $g(H)$ is the shape function for pure Cu (Gaussian) and $l(H)$ is the intensity distribution function of the local fields arising from the conduction-electron spin polarization. In his measurements Sugawara numerically separated the impurity contribution from the total linewidth and showed that $l(H)$ is experimentally well approximated by a cutoff Lorentzian line. The NMR data reported here have been analyzed in the same manner. Below we discuss separately the results for Fe, Cr, Co, and Mn impurities, respectively.

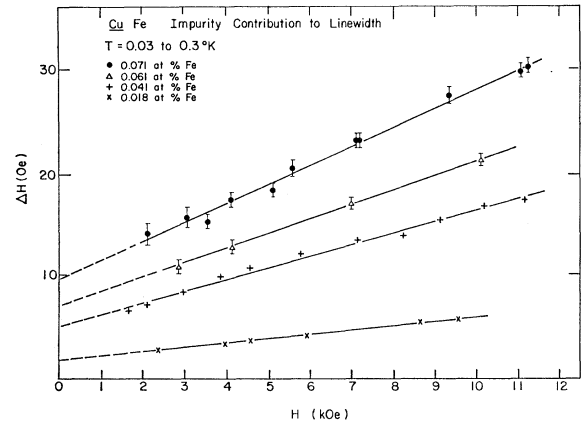

FIG. 4. The impurity contribution to the linewidth data given in Fig. 3, using the analysis described in the text.

A. *Cu*Fe

Various measurements reported recently indicate that Fe in Cu has a Kondo temperature of about 15°K.[11,12,14,23] The total linewidth data for the *Cu*Fe alloys studied are plotted in Fig. 3 as a function of the applied field for fields from 2 to 11 kOe in the temperature range from 0.030 to 0.3°K. Figure 4 shows the impurity contribution to the linewidth versus the applied field, where the impurity contribution ΔH has been obtained as described above. The most important features of these curves are (1) a linewidth from one to two orders of magnitude narrower than the expected linewidth consistent with the high-temperature value of the Fe moment, (2) a field-dependent

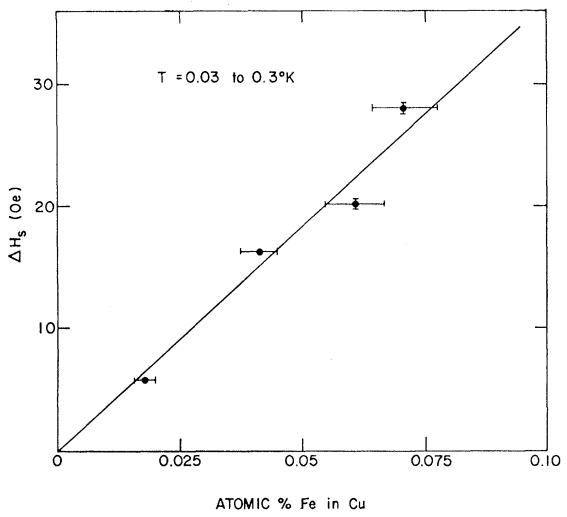

FIG. 5. The dependence of the impurity contribution to the linewidth on Fe concentration for *Cu*Fe. ΔH_s corresponds to the linewidth in 10 kOe.

linewidth in the temperature region where free-spin behavior (Brillouin function) would be independent of field, and (3) a temperature-independent linewidth ($T \ll T_K$) at all fields. The linewidths are the sum of two components, a field-dependent component ΔH_s, which is linear in applied field, and a field-independent component ΔH_0, obtained by extrapolating the data to zero field. Separating these components is complicated, as it involves assumptions concerning the origin of ΔH_0 in order to choose a reasonable line shape (i.e., Lorentzian, Gaussian, etc.). Unfortunately, the data are not sufficiently sensitive to the various possible assumptions to warrant this detailed analysis. Therefore, we write the impurity contribution to the linewidth as

$$\Delta H=\Delta H_0\,|_{H\to 0}+\Delta H_s\,|_{\text{high fields}}. \qquad (6)$$

The linewidth component ΔH_s is linear in Fe concentration (Fig. 5) as expected from the high-temperature data of Sugawara, indicating that ΔH_s does not result from impurity-impurity effects. ΔH_0 depends

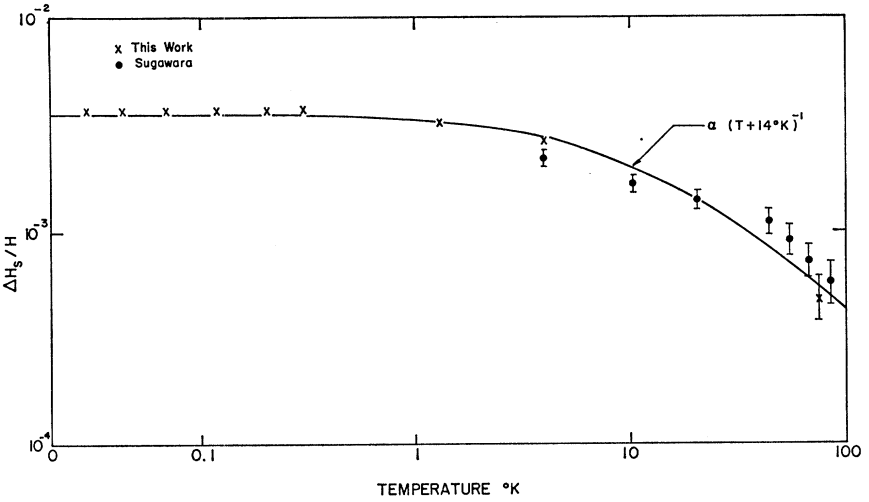

FIG. 6. The temperature dependence of the linewidth component $\Delta H_s/H$ from 0.03 to 85°K for *Cu*Fe. The data of Sugawara (Ref. 25) in the range 1.4 to 85°K are included. Results from different samples are normalized to 0.1 at. % Fe, and Sugawara's data have been normalized to our data at 1.4°K (see text). The data do not fit the free-spin Brillouin function but are well described with a functional form

$$\Delta H_s \propto (T+14)^{-1}.$$

nonlinearly on concentration roughly as $c^{1.5}$. Such behavior may result from a few Fe spins sufficiently close together to be coupled by indirect exchange fields large enough to interfere with the Kondo effect.

The temperature dependence of the linewidth component $\Delta H_s/H$ is plotted in Fig. 6 for temperatures from 0.030 to 85°K, including the data of Sugawara from 1.4 to 85°K. The data have been normalized to a concentration of 0.1 at.% Fe. Sugawara's Fe concentrations have been normalized to ours by comparing his linewidths at 1.4°K with ours. This comparison indicates the "effective" Fe concentration in his samples was roughly 60% of his reported values (relative to our Fe concentrations determined by both chemical analysis and resistivity-ratio measurements as described above). We note in particular that no temperature dependence is observed below 0.5°K. The *Cu*Fe linewidth data obviously cannot be fit with a free-spin Brillouin function, but seems to be of the form $(T+T_K)^{-1}$ with $T_K \simeq 14$°K.[25] The magnetic field is very ineffective in aligning the spin implying the existence of strong spin correlations between the impurity and conduction electrons.

As the applied magnetic field begins to partially break up these spin correlations the z-component of the impurity moment gradually develops as evidenced by the finite low-temperature susceptibility. Various authors[4–7] have reported that $\chi(T)$ can be experimentally fit with an expression of the form

$$\chi = c/(T+\theta) \quad \text{for} \quad T > T_K, \tag{7}$$

where θ is concentration-independent and approximately equal to $2T_K$ as obtained from other measurements. In Fig. 7 we show that the NMR linewidth data is proportional to the impurity contribution to the susceptibility as measured experimentally[26] by Daybell and Steyert[23] and Hurd[16] over the entire temperature range of interest. Therefore, the impurity contribution to the NMR linewidth has the same temperature dependence as $\langle S_z \rangle$. However, above 20°K perturbation theory is known to be valid giving the RKKY spin polarization. Thus we conclude that even as $T \to 0$ and

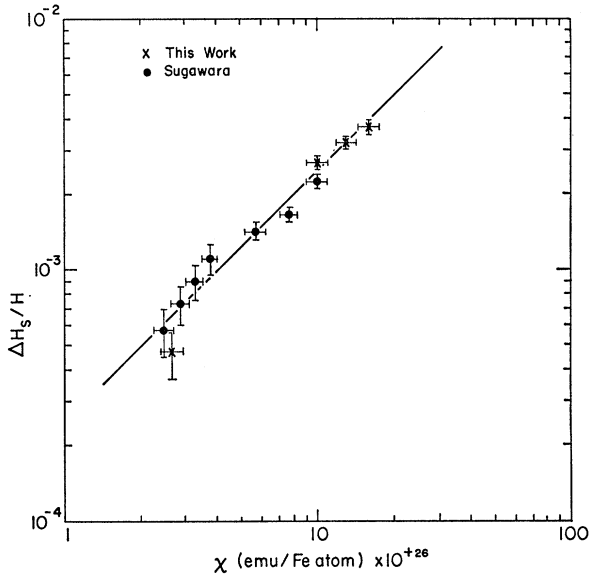

FIG. 7. The impurity contribution to the linewidth as a function of the experimentally measured susceptibility for *Cu*Fe (with temperature as an implicit variable). The solid line has unit slope. The data indicate $\Delta H_s/H$ is proportional to χ.

[25] In an earlier publication (Ref. 11) the authors estimated $T_K \sim 5$°K from NMR. This estimate has proven to be somewhat low. The cause of the low estimate is evident in Fig. 7. The change in slope at 25 kOe brings the NMR estimate of T_K from the magnetic field dependence of the NMR into agreement with other measurements.

[26] The susceptibility data for *Cu*Fe used in Fig. 7 was compiled from the work of Daybell and Steyert (Ref. 23) and that of Hurd (Ref. 16). The data were plotted and a smooth curve drawn without attempting to fit to a single curve of the form $(T+\theta)^{-1}$. The anomalous extra zero-field contribution observed by Daybell and Steyert (Ref. 14) was not included since the NMR data were taken at fields greater than 2 kOe.

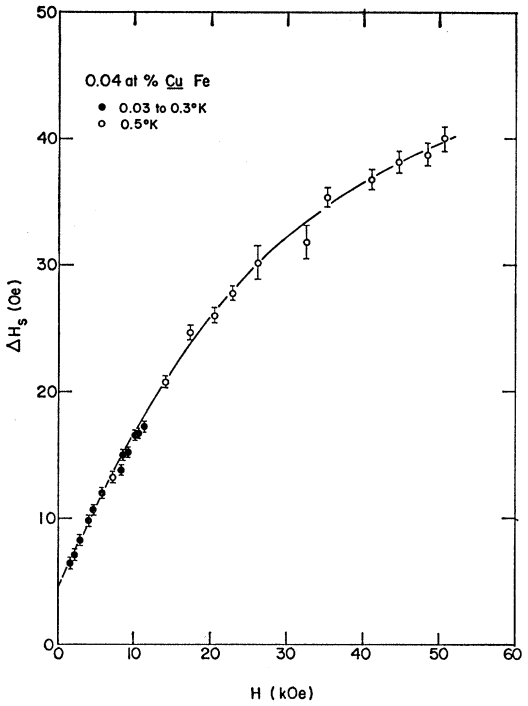

FIG. 8. Magnetic field dependence of the impurity linewidth contribution for magnetic fields up to 50 kOe. The sample contains 0.041 at. % Fe.

the low-temperature spin correlations become important, the RKKY spin polarization around the impurity persists except that the magnitude scales with the true $\langle S_z \rangle$ rather than its free-spin counterpart.

In an attempt to better understand the behavior of the spin correlation in a magnetic field, linewidth measurements on the 0.041 at.% *Cu*Fe alloy were extended to 50 kOe at 0.5°K.[27] The impurity linewidth contribution ΔH_s versus applied field is shown in Fig. 8. Based on the high-temperature linewidth data, the linewidth for this alloy with $\langle S_z \rangle = S$ is (120±5) Oe. The data of Fig. 8 are replotted in Fig. 9 as $\langle S_z \rangle / S$ versus H and combined with the Mossbauer results of Frankel *et al.*[12] by requiring the plot to be continuous. Note the relatively sharp change in slope in the region near 25 kOe.

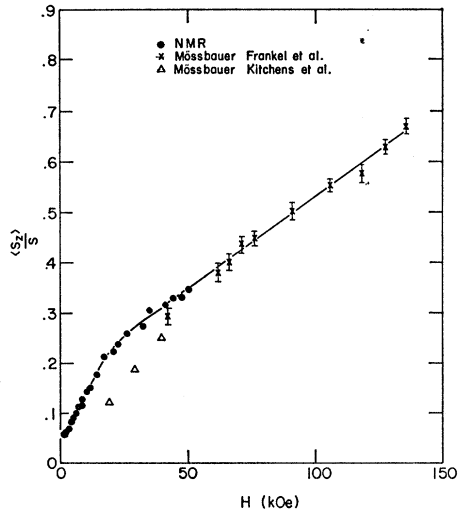

FIG 9. $\langle S_z \rangle / S$ versus H. The data of Fig. 8 are normalized to the value of 120 Oe (based on high-temperature linewidth data) and combined with the Mössbauer results of Frankel *et al.* by requiring the plot to be continuous. Note the change in slope at 25 kOe.

B. *Cu*Cr

The field dependence of the *Cu*Cr alloys at 0.1°K is plotted in Fig. 10. The similarity between this plot and the field dependence of the *Cu*Fe alloy shown in Fig. 9 is striking if the applied fields of Fig. 9 are reduced by a factor of 10. As in the case of *Cu*Fe, linewidths are much narrower than expected from the high-temperature Cr moment and they are linear in field at low field, change slope between 2 and 3 kOe, and then remain essentially linear up to the highest fields investigated. In contrast to the *Cu*Fe system, the *Cu*Cr linewidths show a considerably smaller intercept when they are extrapolated to zero field. This is consistent with the interpretation that ΔH_0 for the *Cu*Fe system results from closely coupled Fe spins, as discussed above, since the Fe concentrations investigated were of necessity larger than the Cr concentrations for the same total linewidth (the Fe susceptibility is smaller). The data presented in Fig. 10 indicate that Cr in Cu forms a Kondo state at low temperatures, with $T_K \approx 1.4$°K. This is confirmed by the temperature dependence of the linewidth at 2 kOe

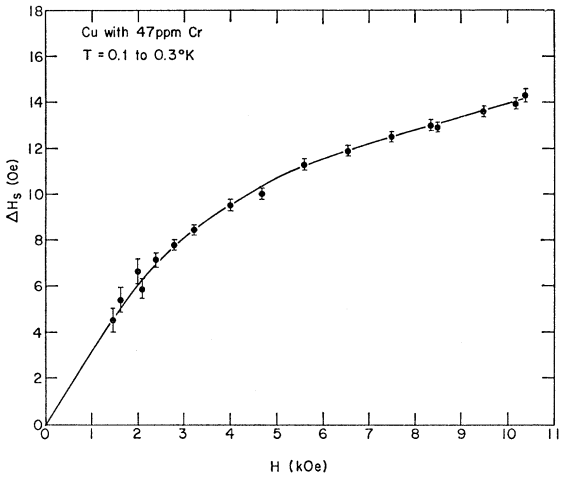

FIG. 10. Magnetic field dependence of the impurity contribution to the linewidth in *Cu*Cr at 0.1°K. There is a change in slope at approximately 2.5 kOe. The sample contains 0.0047 at. % Cr.

[27] We wish to thank Dr. A. Narath and D. C. Barham at the Sandia Laboratory Albuquerque, N.M., for their hospitality in allowing one of us (L. W.) to use their high-field NMR apparatus to order to extend the *Cu*Fe data to 50 kOe.

plotted in Fig. 11. The data do not follow a Brillouin function, but fit a curve of the form $(T+T_K)^{-1}$, with $T_K=1.4$°K. Recent experiments on the transport properties of the *Cu*Cr system indicate a Kondo temperature of around 1°K.[28]

The linewidth in the high-field region behaves differently. The temperature dependence of the linewidths fits a curve of the same type as the low-field data, but with $T_K=2.4$°K (Fig. 11).

Figure 12 shows the field dependence of the linewidths at 0.7°K or a factor of 2 below the Kondo temperature. Clearly, the structure present in the low-temperature data is *not present for temperatures near* T_K, suggesting that the condensation occurs gradually as the temperature is lowered so that the correlated state has not fully formed until $T \ll T_K$.

C. *Cu*Co

No field dependence was observed in the 0.040 at.% *Cu*Co alloy within ±0.2 Oe. This would imply a T_K higher than 1000°K, which is consistent with other data on this system.[14] Perhaps the most useful feature of these data is in establishing an upper limit on the amount of magnetic impurities in a "typical" alloy. This *Cu*Co alloy contained less than 4 ppm Fe, 0.5 ppm Cr, and 0.8 ppm Mn, as estimated from the NMR results themselves.

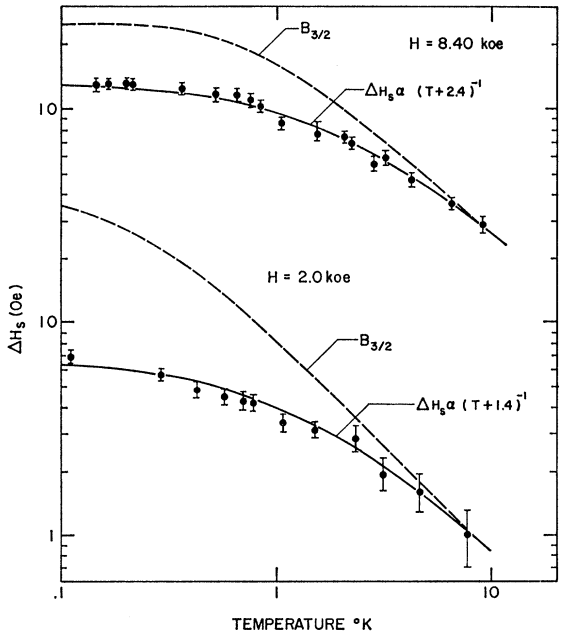

FIG. 11. The temperature dependence of ΔH_s in *Cu*Cr (0.0047 at. %). In 2-kOe external field the data are fit with a form $(T+1.4)^{-1}$; in 8.4 kOe, the corresponding function is $(T+2.4)^{-1}$.

[28] M. Daybell and W. Steyert, Phys. Rev. Letters **20**, 195 (1968).

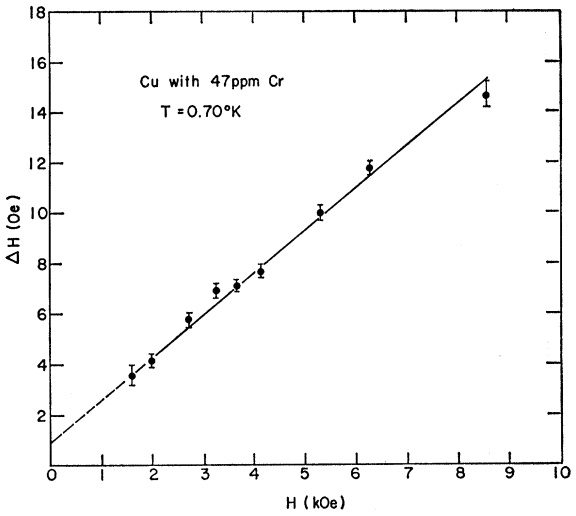

FIG. 12. The magnetic field dependence of ΔH in *Cu*Cr (0.0047 at. %) at 0.7°K. The change in slope evident at lower temperatures (Fig. 10) has disappeared, indicating a gradual formation of the spin correlation.

D. *Cu*Mn

Recent nuclear orientation studies by Campbell *et al.*[21] showed that T_K for Mn in Cu is roughly 0.05°K. With such a low Kondo temperature applied magnetic fields greater than 10^3 G completely disrupt the condensed state ($\mu_B H \gg kT_K$). A self-quenching of the condensed state about each Mn ion is also to be expected from Mn–Mn interactions for sufficiently large concentrations of Mn that short-range order becomes important.

The question of short-range magnetic ordering below a temperature T_S versus the Kondo effect in dilute alloys is itself an interesting one. On the basis of simple energetics one expects that if $T_S \gg T_K$, the internal fields will self-quench the Kondo effect.[22] However, if $T_K \gg T_S$, the spin compensation would be expected to keep the internal fields sufficiently low to prevent ordering. When the two temperatures are comparable, the situation is more complicated.

The *Cu*Mn system was studied in order to determine the effect of short-range order on the Cu NMR. The effects of short range-order on the total magnetization of the alloy have been studied by Careaga *et al.*[29] in a 0.0186 at.% *Cu*Mn alloy. They found no saturation of the magnetization even at 40 kOe at 0.060°K. They postulate a random "antiferromagnetic" state in which small clusters of Mn atoms are locked together by short-range magnetic order and these clusters are then only gradually aligned in an external field. The NMR measurements are a microscopic probe measuring the size of the local fields seen by the Cu nuclei. As the

[29] J. A. Careaga, B. Dreyfus, R. Tournier, and L. Weil, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966* (Proizvodstrenno-Izdatelskii Kombinat, VINITI, Moscow, 1967).

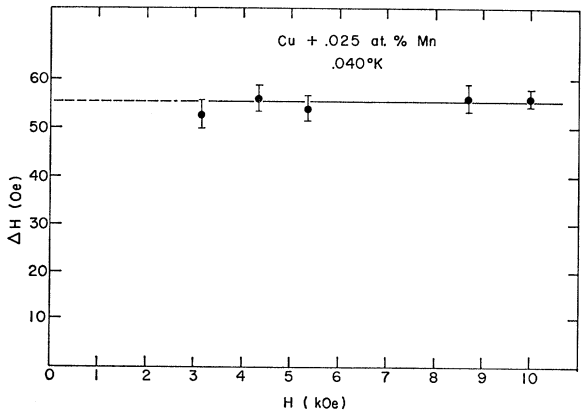

FIG. 13. The impurity contribution to the linewidth in *Cu*Mn (0.02 at. %) as a function of the external field. The data are independent of field in this system where short-range magnetic order is known to be present (see text).

temperature is lowered, each Mn moment will saturate along a local axis of quantization determined by the local magnetic field, i.e., by the external field and the local internal field arising from the conduction-electron polarization due to the other Mn spins in the vicinity. Thus the Mn spins will saturate ($\langle S_z\rangle = S$) along a *local* axis which varies in direction randomly throughout the alloy. Hence for $T < T_s$, the magnitude of the RKKY oscillations will saturate at the maximum value independent of external field yielding large, field-independent linewidths.

Figure 13 shows the Cu^{63} NMR linewidth versus applied field for a 0.02 at.% *Cu*Mn alloy at 0.04°K. The lack of a field-dependent linewidth confirms the above physical arguments.

We note that the data reported for *Cu*Fe and *Cu*Cr are qualitatively different from those for *Cu*Mn. The NMR data are therefore capable of distinguishing between clustering or short-range magnetic order as compared with the low-temperature properties of independent magnetic impurities in a metal.

E. Knight Shift

Although we have not performed additional Knight-shift measurements, we call attention to the precise determinations of the Knight shift in such alloys by Sugawara. He found[24] a small additional temperature-dependent Knight shift at low temperatures for the alloys containing Fe, Cr, or Mn impurities. No satisfactory explanation of these temperature-dependent shifts has been put forward even though it is clear that they are associated with the added Fe, Cr, and Mn impurities.

IV. SUSCEPTIBILITY AND SPIN DENSITY NEAR THE IMPURITY

There has been considerable theoretical effort directed toward understanding the ground state of the magnetic impurity problem. The principal techniques utilized have been many-body perturbation theory,[30–32] self-consistent Green's function[33,34] equations of motion, dispersion theory,[35,36] and calculation with variational singlet wave functions.[6–8] The various techniques seem to arrive at similar conclusions although the detailed point of view may be quite different. However, Silverstein and Duke[37,38] have shown the Green's-function theories and Suhl's dispersion theory as well as the perturbation theory attempts of Abrikosov[30] and Yosida[6,32] to be limited to logarithmic accuracy; i.e., they do not reproduce the lower-order logarithmic divergences in perturbation theory. The effect of this limitation is not yet clear, but it may strongly influence the calculated low-temperature properties. Of the variational singlet approaches,[6–8] the ground-state function proposed by Heeger and Jensen[7] and that proposed by Kondo[8] and developed by Applebaum and Kondo[8] (AK) are quite similar. (The spin correlations included are identical.) However, the AK theory preserves electron-hole symmetry from the outset and spatially correlates the Fermi sea into scattering states orthogonal to the quasiparticle state which is itself correlated into a singlet with the impurity. This extra correlation results in a considerably larger binding energy. Anderson[39] has also studied a singlet-type variational wave function. Although his starting function is somewhat more general than AK when it is applied to the *s-d* model Anderson's variational function is the same as that of AK.

Of the various physical properties which have been calculated, there is a general agreement on the resistivity approaching and remaining at the unitarity limit at low temperatures. Consequently, the transport properties do not seem to provide a critical test of the proper low-temperature treatment. (This is perhaps less true of the magnetoresistance.) On the other hand, the specific heat does seem to provide such a test. The low-temperature AK theory predicts[8]

$$\Delta C \sim T \ln(T/T_K),$$

whereas the Green's-function calculations of Bloomfield and Hamann[40] numerically are approximated by

$$\Delta C \sim T^{1/2}.$$

[30] A. Abrikosov, Physics **2**, 5 (1965).
[31] J. Kondo, Phys. Rev. **154**, 644 (1967).
[32] K. Yosida and A. Okiji, Progr. Theoret. Phys. (Kyoto) **34**, 505 (1965); A. Okiji, *ibid.* **36**, 875 (1966).
[33] S. Doniach, Phys. Rev. **144**, 382 (1966).
[34] F. Takano and T. Ogawa, Progr. Theoret. Phys. (Kyoto) **35**, 343 (1966).
[35] H. Suhl, Phys. Rev. **138**, 515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966).
[36] H. Suhl and D. Wong, Physics **3**, 17 (1967).
[37] S. D. Silverstein and C. B. Duke, Phys. Rev. Letters **18**, 695 (1967).
[38] S. D. Silverstein and C. B. Duke, Phys. Rev. **161**, 456 (1967).
[39] P. W. Anderson, Phys. Rev. **164**, 352 (1967).
[40] P. E. Bloomfield and D. R. Hamann, Phys. Rev. **164**, 856 (1967).

The Green's-function theory formulated by Takano and Ogawa[34] and developed by Zuckerman and Celli[41] and Klein[42] give a low-temperature specific heat of the form

$$\Delta C \sim T.$$

The experimental data seem to be in agreement with the AK result as shown in Figs. 14 and 15. In Fig. 14 we plot the low-temperature data obtained by Franck, Manchester, and Martin on the *Cu*Fe system and tabulated in their 1961 paper.[18] Note that there are two effects:

(1) There is an apparent change in γ, the coefficient of the linear term.

(2) There is an upturn in C/T at low temperature, which is clearly outside of the limits of error.

In expectation of ln T behavior, we plot in Fig. 15 the difference between the actual points and the upper straight line of Fig. 14 as a function of $(-\ln T)$. The resulting straight line confirms the logarithmic dependence. From Figs. 14 and 15 we find the excess specific heat to be of the form

$$\Delta C = \delta(T \ln T_K - T \ln T),$$

where $T_K = 10°\text{K}$ (δ can be obtained from the slope of the ln$T$ graph and has the value 4.5×10^{-4}). This value of T_K is in good agreement with all other measurements. The specific heat therefore suggests that the AK theory may provide the essential features of the many-body ground state. The data of Figs. 14 and 15 come from the 0.05%-Fe sample studied by Franck, *et al.* Unfortunately this concentration is the only one studied that is sufficiently dilute to be assured of solubility and free of impurity interactions. The higher-concentration data are definitely concentration-dependent. Admittedly, more specific-heat data at lower temperatures and lower concentrations are needed to confirm this result, but the tentative conclusion is definitely in favor of the AK theory. We shall see that the resonance data presented here lends further support.

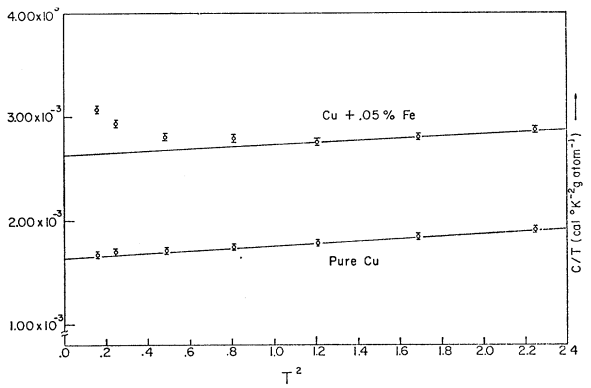

FIG. 14. The tabulated data of Franck, Manchester, and Martin (Ref. 18) plotted as C/T versus T^2 for pure Cu and Cu+0.05 at. % Fe. Note the upturn in the data at the lowest temperatures for the sample containing Fe. The error bars are included as given by Franck, Manchester, and Martin.

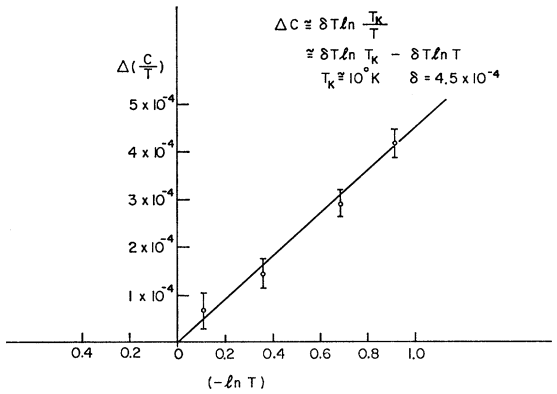

FIG. 15. $(\Delta C/T)$ versus $(-\ln T)$. The difference between the actual points and the upper straight line of Fig. 14 are plotted as a function of $(-\ln T)$. The resulting straight line confirms the logarithmic dependence.

In this section we calculate the magnetic susceptibility of the AK singlet at 0°K and work out the conduction-electron spin density in the vicinity of a partially polarized impurity. It was argued in Sec. III that the NMR results indicated the RKKY form of the spin polarization persists even in the low-temperature limit. This experimental result presents one with an apparent paradox. On the one hand it is clear that a nonperturbative theory is required; and on the other, one finds the RKKY perturbative result gives a good answer. Thus one is faced with the need to use the *s-d* interaction first to form a new ground state and then again to obtain the spin polarization around a polarized impurity. It is immediately evident that a AK-type theory is needed; namely, one where a *part* of the *s-d* Hamiltonian is treated exactly, leading to a nonperturbative ground state; while the remainder of the *s-d* Hamiltonian is then treated perturbatively, leading to results of the RKKY form. We show here that this is indeed the case for the AK singlet, but find in addition a new long-range spin-polarization characteristic of the ground state.

The transformed AK Hamiltonian may be written in the form[8]

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2, \tag{8}$$

where

$$\mathcal{H}_0 = \sum_{l,\sigma(l\neq 0)} \lambda_l a_{l\sigma}^\dagger a_{l\sigma} + (|J|/N) f_0^2 [a_{0\sigma}^\dagger a_{0\sigma'} (\mathbf{S}\cdot\mathbf{s})_{\sigma\sigma'}], \tag{9}$$

$$\mathcal{H}_1 = (g\mu_B/N) \sum_{\mathbf{k},\mathbf{q}} \tfrac{1}{2} (C_{\mathbf{k}+\mathbf{q}\uparrow}^\dagger C_{\mathbf{k}\uparrow} - C_{\mathbf{k}+\mathbf{q}\downarrow}^\dagger C_{\mathbf{k}\downarrow}) H(\mathbf{q}) + (g'\mu_B/N) S_z \sum_{\mathbf{q}} H(\mathbf{q}), \tag{10}$$

$$\mathcal{H}_2 = (|J|/N) \sum_{l,l';\sigma,\sigma'} f_l f_{l'} a_{l\sigma}^\dagger a_{l'\sigma'} (\mathbf{S}\cdot\mathbf{s})_{\sigma\sigma'} + \sum_{l,\sigma,\sigma'} T_{\sigma\sigma'}(l) (a_{l\sigma}^\dagger a_{0\sigma'} + a_{0\sigma}^\dagger a_{l\sigma'}), \tag{11}$$

[41] V. Celli and M. J. Zuckerman, Phys. Letters **25A**, 305 (1967).
[42] A. Klein, Phys. Letters **26A**, 57 (1967).

where

$$T_{\sigma\sigma'}(l)=\tfrac{1}{2}\mu_l\delta_{\sigma\sigma'}+(|J|/N)f_lf_0(\mathbf{S}\cdot\mathbf{s})_{\sigma\sigma'}.$$

The $a_l^\dagger$ and $C_k^\dagger$ operators are related via the AK canonical transformation

$$a_{l\sigma}^\dagger=\sum_k p_{lk}C_{k\sigma}^\dagger,$$
$$a_{0\sigma}^\dagger=\sum_k p_{0k}C_{k\sigma}^\dagger, \qquad (12)$$

where

$$p_{0k}=\frac{(\epsilon_B/2\rho)^{1/2}}{|\epsilon_k|+\epsilon_B};$$
$$p_{lk}=\mu_l p_{0k}/2(\epsilon_k-\lambda_l).$$

The Lagrange multiplier μ_l is evaluated in AK. J is the s-d exchange coupling constant, and the conduction-electron energies λ_l as well as the coefficients f_l are as defined by AK. The Hamiltonian $\mathcal{H}_0$ defines the variational ground state through the Schrödinger equation

$$\mathcal{H}_0|G\rangle=-\epsilon_B|G\rangle,$$

where

$$|G\rangle=(1/\sqrt{2})(a_{0\downarrow}^\dagger\alpha-a_{0\uparrow}^\dagger\beta)\prod_{l=1}^{N/2}a_{l\uparrow}^\dagger a_{l\downarrow}^\dagger|\text{vac}\rangle,$$

where α and β are the usual spin-$\frac{1}{2}$ eigenfunctions with eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively. ϵ_B is the condensation energy of the system. The term $\mathcal{H}_1$ represents the interaction with the external magnetic field. In $\mathcal{H}_1$ we allow the conduction-electron and local spin-g values to differ and note that the interaction with the spin is local. The final term $\mathcal{H}_2$ represents that part of the s-d Hamiltonian not included in $\mathcal{H}_0$. AK attempt to show that this term may be treated by perturbation theory on the variational ground state without altering the exponent of the nonanalytic binding energy. Following this approach we shall calculate the susceptibility for a system described by $\mathcal{H}_0+\mathcal{H}_1$ and leave the perturbation Hamiltonian $\mathcal{H}_2$ to be treated subsequently.

We define the spin-density operator

$$\Theta_{kq}\equiv C_{k+q\uparrow}^\dagger C_{k\uparrow}-C_{k+q\downarrow}^\dagger C_{k\downarrow} \qquad (13)$$

and wish to consider the equations of motion of the operators Θ_{kq} and S_z.

$$i\dot{\Theta}_{kq}=[\Theta_{kq},\mathcal{H}_0+\mathcal{H}_1], \qquad (14)$$
$$i\dot{S}_z=[S_z,\mathcal{H}_0+\mathcal{H}_1]. \qquad (15)$$

Evaluation of the commutators is given in Appendix A leading to the results

$$i\dot{\Theta}_{kq}=\sum_{ll'}p_{l\,k+q}p_{l'k}(\lambda_{l'}-\lambda_l)[a_{l\uparrow}^\dagger a_{l'\uparrow}-a_{l\downarrow}^\dagger a_{l'\downarrow}]$$
$$+2(|J|/N)f_0^2p_{0\,k+q}p_{0k}[S^-a_{0\uparrow}^\dagger a_{0\downarrow}-S^+a_{0\downarrow}^\dagger a_{0\uparrow}]$$
$$+\tfrac{1}{2}(g\mu_B/N)H(q)(n_{k+q}'-n_k')+\tfrac{1}{2}(g\mu_B/N)$$
$$\times\sum_p H(p)(p_{0\,k+q}p_{0\,k-p}-p_{0\,k+q+p}p_{0k})(a_{0\uparrow}^\dagger a_{0\uparrow}$$
$$+a_{0\downarrow}^\dagger a_{0\downarrow}). \qquad (16)$$

In (16) the quantities n_k', n_{k+q}' are the number operators [see Eq. (A5)]

$$i\dot{S}_z=(|J|/N)f_0^2[S^+a_{0\downarrow}^\dagger a_{0\uparrow}-S^-a_{0\uparrow}^\dagger a_{0\downarrow}]. \qquad (17)$$

Taking expectation values and assuming steady-state conditions one obtains from (16) and (17)

$$0=\sum_{ll'}p_{l\,k+q}p_{l'k}(\lambda_{l'}-\lambda_l)\langle a_{l\uparrow}^\dagger a_{l'\uparrow}-a_{l\downarrow}^\dagger a_{l'\downarrow}\rangle$$
$$+(g\mu_B/2N)H(q)(\bar{n}_{k+q}'-\bar{n}_k')+\tfrac{1}{2}(g\mu_B/N)$$
$$\times\sum_p H(p)(p_{0\,k+q}p_{0\,k-p}-p_{0\,k+q+p}p_{0k})$$
$$\times\langle a_{0\uparrow}^\dagger a_{0\uparrow}+a_{0\downarrow}^\dagger a_{0\downarrow}\rangle, \qquad (18)$$
$$0=\langle S^+a_{0\downarrow}^\dagger a_{0\uparrow}-S^-a_{0\uparrow}^\dagger a_{0\downarrow}\rangle. \qquad (19)$$

In the above, the expectation values are taken with respect to the perturbed wave function in the magnetic field, except that since we desire only the linear term in the response, the quantities $\bar{n}_k'$ are to be evaluated in the zero-field ground state. Equation (18) is analogous to Wolff's result[43] for the free-electron gas and leads to the conduction-electron susceptibility.

We proceed by considering the operator

$$\alpha_0\equiv S^+a_{0\downarrow}^\dagger a_{0\uparrow}-S^-a_{0\uparrow}^\dagger a_{0\downarrow}. \qquad (20)$$

From (19), $\langle\alpha_0\rangle=0$ and

$$\langle\dot{\alpha}_0\rangle=0 \qquad (21)$$

under the same steady-state conditions. The equation of motion for α_0 may be written

$$i\dot{\alpha}_0=[\alpha_0,\mathcal{H}_0+\mathcal{H}_1]. \qquad (22)$$

Evaluation of the commutator is straightforward, leading to

$$i\dot{\alpha}_0=(|J|/N)f_0^2[-(a_{0\uparrow}^\dagger a_{0\uparrow}-a_{0\downarrow}^\dagger a_{0\downarrow})+2S_z(a_{0\uparrow}^\dagger a_{0\uparrow}$$
$$+a_{0\downarrow}^\dagger a_{0\downarrow})-4S_za_{0\uparrow}^\dagger a_{0\downarrow}^\dagger a_{0\downarrow}a_{0\uparrow}]-(g'\mu_B/N)$$
$$\times\sum_q H(q)[S^+a_{0\downarrow}^\dagger a_{0\uparrow}+S^-a_{0\uparrow}^\dagger a_{0\downarrow}]+\tfrac{1}{2}(g\mu_B/N)$$
$$\times[\sum_{k,q}[\sum_l p_{0k}p_{l\,k+q}(S^-a_{l\uparrow}^\dagger a_{0\downarrow}+S^+a_{l\downarrow}^\dagger a_{0\uparrow})$$
$$+\sum_l p_{0\,k+q}p_{lk}(S^-a_{0\uparrow}^\dagger a_{l\downarrow}+S^+a_{0\downarrow}^\dagger a_{l\uparrow})]H(q)]. \qquad (23)$$

Once again we take expectation values in the perturbed state, keeping only lowest-order terms in $H(q)$. Thus the operators multiplied by $H(q)$ are evaluated in the zero-field ground state, using

$$\langle G|S^+a_{l\downarrow}^\dagger a_{0\uparrow}|G\rangle=\langle G|S^-a_{l\uparrow}^\dagger a_{0\downarrow}|G\rangle=-\tfrac{1}{2}\delta_{l0}. \qquad (24)$$

Then, from (21),

$$0=(|J|/N)f_0^2[-\langle(a_{0\uparrow}^\dagger a_{0\uparrow}-a_{0\downarrow}^\dagger a_{0\downarrow})\rangle$$
$$+2\langle S_z(a_{0\uparrow}^\dagger a_{0\uparrow}+a_{0\downarrow}^\dagger a_{0\downarrow})\rangle-4\langle S_za_{0\uparrow}^\dagger a_{0\downarrow}^\dagger a_{0\downarrow}a_{0\uparrow}\rangle]$$
$$-(g\mu_B/N)\sum_{k,q}p_{0k}p_{0\,k+q}H(q)+(g'\mu_B/N)\sum_q H(q). \qquad (25)$$

[43] P. Wolff, Phys. Rev. **120**, 814 (1960).

We truncate the equations by factorizing the quantities

$$\langle S_z(a_{0\uparrow}{}^\dagger a_{0\uparrow}+a_{0\downarrow}{}^\dagger a_{0\downarrow})\rangle \cong \langle S_z\rangle, \tag{26}$$

$$\langle S_z a_{0\uparrow}{}^\dagger a_{0\downarrow}{}^\dagger a_{0\downarrow} a_{0\uparrow}\rangle = 0. \tag{27}$$

The above is the lowest-order factorization leading to a nonzero result and should give the linear term in $H(q)$ correctly. Equation (25) becomes

$$2\langle S_z\rangle - \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle = -(g'\mu_B/|J|f_0^2) \times \sum_q H(q) + (g\mu_B/|J|f_0^2) \sum_{k,q} p_{0k}p_{0\,k+q}H(q). \tag{28}$$

Consider now the effect of a δ-function field at the origin; i.e.,

$$H(q) = h \qquad \text{for all } q.$$

Then

$$2\langle S_z\rangle - \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle = [-g'\mu_B h\delta(\mathbf{r}) + g\mu_B h A(\mathbf{r})](|J|f_0^2)^{-1}. \tag{29}$$

The function $A(\mathbf{r})$ is evaluated in Appendix B and is given by

$$A(\mathbf{r}) = \sum_{\mathrm{k,k'}} p_{0k}p_{0k'} \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]. \tag{30}$$

Thus, from the spatial dependence of (29), as well as the g values, we identify

$$2\langle S_z\rangle = -(g'\mu_B/N) \sum_q H(q)(N/|J|f_0^2), \tag{31}$$

$$\langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle = -(g\mu_B/N) \times \sum_{k,q} p_{0k}p_{0\,k+q}H(q)(N/|J|f_0^2). \tag{32}$$

Equation (31) gives the spin polarization of the local moment and (32) gives that of the quasiparticle. Note that in a uniform external field

$$H(q) = H_0\delta(q).$$

Equation (28) reduces to

$$2\langle S_z\rangle - \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle = \Delta g\mu_B H_0/|J|f_0^2, \tag{33}$$

so that in a uniform field the two contributions are identical when $g'=g$. Using the results of AK for f_0, (31) and (32) become

$$\langle S_z\rangle = \frac{-g'\mu_B}{\frac{4}{3}kT_K \ln(D/kT_K)} \sum_q H(q), \tag{34}$$

$$\tfrac{1}{2}\langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle = \frac{-g\mu_B}{\frac{4}{3}kT_K \ln(D/kT_K)} \times \sum_{k,q} p_{0k}p_{0\,k+q}H(q), \tag{35}$$

where $kT_K = \epsilon_B$, the condensation energy.

Returning to the conduction-electron contribution to the susceptibility, Eq. (19) can be put in the form (see Appendix C)

$$0 = (\epsilon_k - \epsilon_{k+q})[\langle\theta_{kq}\rangle - p_{0k}p_{0\,k+q}\langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle] + \tfrac{1}{2}(g\mu_B/N)H(q)(\bar{n}_{k+q}{}' - \bar{n}_k') + \tfrac{1}{2}(g\mu_B/N) \times \sum_p H(p)(p_{0\,k+q}p_{0\,k-p} - p_{0\,k+q+p}p_{0k}) \times \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} + a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle. \tag{36}$$

The conduction-electron spin polarization is therefore

$$\langle\sigma_z(q)\rangle = \tfrac{1}{2}\sum_k \langle\theta_{kq}\rangle = -\tfrac{1}{4}(g\mu_B/N)H(q)F(q) + \tfrac{1}{2}\langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle \times \sum_k p_{0k}p_{0\,k+q} - \tfrac{1}{4}(g\mu_B/N) \sum_p H(p)G(p,q) \times \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} + a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle, \tag{37}$$

where

$$F(q) \equiv -\sum_k [(\bar{n}_{k+q}{}' - \bar{n}_k')/(\epsilon_{k+q} - \epsilon_k)],$$

$$G(p,q) \equiv -\sum_k \frac{p_{0\,k+q}p_{0\,k-p} - p_{0\,k+q+p}p_{0k}}{\epsilon_{k+q} - \epsilon_k}. \tag{38}$$

The function $F(q)$ is the counterpart of the RKKY function for the free-electron gas.[43] It differs by an amount which is of order $1/N$ since the occupation numbers $\bar{n}_k'$ differ slightly from those of the electron gas without impurity. The resulting correction to the susceptibility is of order $(1/N)\chi_p$, where χ_p is the free-electron susceptibility. Consequently, as long as $T_k \ll T_F$, we may replace $F(q)$ by the free-electron function. The contribution from $G(p,q)$ vanishes for $p=0$ and so does not change the bulk susceptibility. For a delta function $\delta(r)$ field we integrate over p, giving

$$G(q) = \sum_p G(p,q) = \sum_k [(p_{0\,k+q} - p_{0k})f_0/(\epsilon_{k+q} - \epsilon_k)],$$

where f_0 is the summation over p of p_{0p}. Thus f_0 factors out of $G(q)$ and then upon the k summation $G(q)$ vanishes. This is clear since $G(q)$ is analogous to a free-electron $F(q)$ for a filled band with the shape described by p_{0k}.

From Eqs. (37) and (34) we obtain for the total static susceptibility in a uniform field

$$\chi = \chi_{\mathrm{Pauli}} + \frac{2g^2\mu_B{}^2}{\frac{4}{3}kT_K \ln(D/kT_K)}. \tag{39}$$

The result is in agreement with experiment, which shows a finite $T\to 0$ susceptibility of this order of magnitude. The remainder of the Hamiltonian $\mathcal{H}_2$ is included by noting that it represents virtually the entire s-d exchange term except for a very narrow region of energies near E_F which was put into $\mathcal{H}_0$. We shall treat $\mathcal{H}_2$ by a molecular-field approximation and replace all impurity spin operators by their average

values in the external field, leaving the conduction-electron operators in the usual manner. In this approximation

$$\mathcal{H}_2=(|J|/N)\langle S_z\rangle[\sum_{ll'}f_lf_{l'}(a_{l\uparrow}{}^\dagger a_{l'\uparrow}-a_{l\downarrow}{}^\dagger a_{l'\downarrow})+\sum_{l\neq 0}f_lf_0[(a_{l\uparrow}{}^\dagger a_{0\uparrow}-a_{l\downarrow}{}^\dagger a_{0\downarrow})+(a_{0\uparrow}{}^\dagger a_{l\uparrow}-a_{0\downarrow}{}^\dagger a_{l\downarrow})]]. \tag{40}$$

Adding and subtracting the term

$$(|J|/N)\langle S_z\rangle f_0^2(a_{0\uparrow}{}^\dagger a_{0\uparrow}-a_{0\downarrow}{}^\dagger a_{0\downarrow}),$$

we may write

$$\begin{aligned}\mathcal{H}_2&=(|J|/N)[\sum_{\mathbf{k},\mathbf{q}}(C_{\mathbf{k}+\mathbf{q}\uparrow}{}^\dagger C_{\mathbf{k}\uparrow}-C_{\mathbf{k}+\mathbf{q}\downarrow}{}^\dagger C_{\mathbf{k}\downarrow})-f_0^2(a_{0\uparrow}{}^\dagger a_{0\uparrow}-a_{0\downarrow}{}^\dagger a_{0\downarrow})]\langle S_z\rangle\\&=(|J|/N)\langle S_z\rangle[\sum_{\mathbf{k},\mathbf{q}}(1-f_0^2p_{0k}p_{0\,k+q})\times(C_{\mathbf{k}+\mathbf{q}\uparrow}{}^\dagger C_{\mathbf{k}\uparrow}-C_{\mathbf{k}+\mathbf{q}\downarrow}{}^\dagger C_{\mathbf{k}\downarrow})]\\&=|J|\langle S_z\rangle s_z\delta(\mathbf{r})-(|J|/N)\langle S_z\rangle f_0^2A(\mathbf{r})s_z\\&=g\mu_B\mathbf{s}\cdot\tilde{H}(r).\end{aligned}$$

The effective field is given by

$$\tilde{H}(\mathbf{r})=\langle S_z\rangle(|J|/g\mu_B)\delta(\mathbf{r})-(|J|/Ng\mu_B)f_0^2A(\mathbf{r})\langle S_z\rangle. \tag{41}$$

The response may be obtained directly from Eq. (37):

$$\begin{aligned}\langle\sigma(\mathbf{r})\rangle&=-\tfrac{1}{4}g\mu_BN(0)H_0+\tfrac{1}{2}\langle a_{0\uparrow}{}^\dagger a_{0\uparrow}-a_{0\downarrow}{}^\dagger a_{0\downarrow}\rangle A(\mathbf{r})\\&\quad-\tfrac{1}{4}(|J|/N)\sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})F(\mathbf{q})\langle S_z\rangle+\tfrac{1}{4}(|J|f_0^2/N^2)\times\sum_{\mathbf{k},\mathbf{q}}p_{0k}p_{0\,k+q}\exp(i\mathbf{q}\cdot\mathbf{r})F(\mathbf{q})\\&=-\tfrac{1}{2}g\mu_BN(0)H_0-\tfrac{1}{4}(|J|/N)\langle S_z\rangle\times\sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})F(\mathbf{q})+\langle S_z\rangle\times[1+(|J|f_0^2/N^2)N(0)]A(\mathbf{r}).\end{aligned} \tag{42}$$

Thus we obtain the spin density

$$\langle\sigma(\mathbf{r})\rangle=\sigma_0+\sigma(\mathbf{r})\,|_{\mathrm{RKKY}}+\langle S_z\rangle(1+\tfrac{1}{18}(\epsilon_B/|J|))A(\mathbf{r}), \tag{43}$$

where σ is the uniform polarization, $\sigma(r)\,|_{\mathrm{RKKY}}$ is the usual RKKY result, and the final term is an additional very long-range spin polarization which is oscillatory but *always negative*.

Thus the nuclei should be affected as follows:

(1) From σ_0 one expects the usual Knight shift.

(2) From $\sigma\,|_{\mathrm{RKKY}}$ one expects oscillatory Knight shifts which lead to no net shift of the line; only a width proportional to $\langle S_z\rangle$.

(3) From the final term one expects some additional broadening; but the predominent effect would be a small shift of the line since this contribution is always of the same sign. Thus one expects a small additional Knight shift proportional to $\langle S_z\rangle$.

These contributions will be estimated in the following section and compared with experiment for the Cu alloys studied experimentally in this paper.

In the above analysis we have completely neglected the potential scattering associated with the impurity as considered by AK. This neglect is not serious for the effect of mean free path on the RKKY spin-density oscillations is well known[44] and results simply from the smearing of the Fermi surface in k space, leading to an exponential damping. Since the mean free path can be made arbitrarily long for sufficiently dilute alloys this can be made experimentally not very important. However, it should be remembered that both of the range functions are mean-free-path limited.

V. DISCUSSION

The magnetic susceptibility and spin polarization calculated in the previous section are in general agreement with experiment. The low-temperature susceptibility is temperature-independent,[14–17] and seems to scale as T_K^{-1} as given by Eq. (39). The coefficient is difficult to check quantitatively at this point since the theory is strictly valid only for spin $\frac{1}{2}$. It has been speculated[39] that the low-temperature susceptibility would diverge as $T^{-1/2}$ or possibly $\ln T$. These suggestions are based on relating the susceptibility and the electronic specific heat (γT) via an expression

$$\chi\propto\gamma,$$

such as is valid for the free-electron case.

Such a connection is not at all obvious. In fact, although the electron-phonon interaction in metals can lead to a large enhancement of the electronic specific heat, it does not affect the spin susceptibility.[45,46] Very simply, one may think of the enhancement as a many-body "bump" on the density-of-states curve. However, this "bump" is tied to the Fermi surface, and therefore does not participate in the spin-up–spin-down population difference which gives the spin susceptibility. We speculate that a similar situation occurs here, for the calculation shows no sign of a zero temperature divergence in χ.

It should be noted that Daybell and Steyert have observed a low-temperature contribution[14] to χ which can be fit reasonably by $T^{-1/2}$. However, they find that very low fields (<1 kOe) are sufficient to saturate and remove this contribution. We suggest that this ano-

[44] A. J. Heeger, A. Klein, and P. Tu, Phys. Rev. Letters **17**, 803 (1966).

[45] For a discussion, see C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV, p. 290.

[46] M. J. Buckingham, Nature **168**, 281 (1951).

malous contribution might be the result of a few Fe spins sufficiently close together to be coupled by indirect exchange fields large enough to interfere with the Kondo state. There is some evidence in the *Cu*Fe NMR results to support this as described in Sec. III. From this point of view the low-temperature susceptibility of the *Cu*Cr system (where there is essentially no zero-field contribution to the linewidth) will be of interest.

The existence of RKKY spin-density oscillations as predicted by Eq. (43) seems established by the NMR data for both the *Cu*Fe and the *Cu*Cr systems. This is an important result which follows quite naturally from the AK theory of the ground state.

The field dependence of $\langle S_z\rangle$ as measured by the NMR and Mössbauer data is particularly interesting. The relatively sharp change in slope observed in both *Cu*Fe and *Cu*Cr has not yet been explained although it is clear that there are many nonlinear terms which were dropped in the susceptibility calculation of Sec. IV. The data for the two different impurities is quite similar when scaled to T_K except the change in slope is larger for the Cr than the Fe. One would also expect the kink to show up in the bulk susceptibility.

Nam and Woo[47] have calculated the field dependence of the susceptibility using the variational singlet developed by Heeger and Jensen.[7] Although their results are in rough agreement with the experiments they found no anomalous low-field change in slope.

In addition to the RKKY result, Eq. (43) predicts new a long-range spin polarization of the form

$$\sigma(r)=A\left((\sin k_F r)/k_F r\right)^2. \tag{44}$$

Such a long-range spin polarization has many obvious consequences; and if present should be observable. We focus our attention in particular on the Knight shift. Since the polarization has a fixed sign it will clearly cause a shift in the center of mass of the NMR line (there will also be an extra contribution to the width of the same magnitude as the shift.) We estimate this shift for *Cu*Fe. From Eq. (B10) (Appendix B) the range function may be written for *Cu*Fe:

$$A(r)=3N(kT_K/E_F)\left((\sin k_F r)/k_F r\right)^2$$
$$\simeq N10^{-20}/r^2. \tag{45}$$

In obtaining (45) we assume a free-electron model for the 4*s* band of Cu, with $E_F=7$ eV, $k_F=1.4\times10^8$ cm^{-1}, and $(\sin^2 k_F r)\simeq\frac{1}{2}$. Such a spin polarization in the Cu 4*s* band produces a hyperfine field at the Cu nucleus of order 2×10^6 Oe per spin, so that the estimated contribution to the hyperfine field is

$$H_N=N^{-1}(A_N/g_N\mu_N)A(r)(\langle S_z\rangle/S). \tag{46}$$

Putting in the experimental number of $\langle S_z\rangle/S\simeq10^{-1}$ in 10^4 G for *Cu*Fe we estimate

$$\Delta H_N\simeq 2\times10^{-15}/r^2 \text{ Oe}. \tag{47}$$

In order to obtain the total shift in the line one must sum up the contributions to hyperfine field at a particular site from all nearby impurities. In fact, the above expression for $A(r)$ is valid only for distances $r<\xi$, where ξ is the coherence length $[\xi_0=(2/k_F)(E_F/kT_K)]$,[7-9] so that only impurities within such a distance contribute. However, as argued above, there is a second limitation on the range; the mean free path λ. We have not attempted a detailed calculation of the effect of mean free path on this long-range polarization, but it seems physically clear that the long-range coherence cannot persist beyond λ. This certainly is the case in superconductivity where the coherence length is λ limited. In fact, it has been demonstrated quite generally that the density-density correlation function in an impure metal falls off exponentially as $\exp(-r/\lambda)$.[48] Consequently, the quasiparticle wave function is similarly bounded. We conclude that the total shift is obtained by summing over all impurities within roughly a coherence length or a mean free path, whichever is smaller. The resulting extra Knight shift estimated for *Cu*Fe is

$$\Delta K\simeq 8\pi cN\times10^{-19}\left(\frac{\xi}{\lambda}\right), \tag{48}$$

where ξ or λ is to be inserted depending on the conditions. For 0.04% Fe the mean free path may be estimated using a free-electron model for the resistivity (15 $\mu\Omega$ cm/at.%)[13] as 10^{-5} cm. This is also approximately the estimated value of ξ. Thus one expects an excess low-temperature Knight shift of about 0.06%. The actual result as measured by Sugawara[24] is of order 0.01 to 0.02%. Considering the crudeness of the estimate at all stages the agreement is not bad. In particular the upper limit ξ is not precisely defined, and the experimental coherence length ξ may be somewhat smaller than ξ_0. The data show that ΔK increases as the temperature is lowered to 15°K and stays approximately constant for lower temperatures, thus scaling with the temperature dependence of $\langle S_z\rangle$. A similar shift is found experimentally for *Cu*Cr. We conclude that there are low-temperature shifts as predicted and of approximately the correct magnitude.

A somewhat larger shift has been observed by Narath, Gossard, and Wernick[49] for the system *Au*V ($T_K\simeq$ 300°K[17]). Because of the large value for T_K and the high solubility of V in Au, it was possible to study the V^{51} NMR up to concentrations of 10%V. There are two aspects of the data of particular interest (see

[47] S. B. Nam and J. W. F. Woo, Phys. Rev. Letters **19**, 649 (1967).

[48] P. R. Weiss and E. Abrahams, Phys. Rev. **111**, 722 (1958).

[49] A. Narath, A. C. Gossard, and J. H. Wernick (to be published).

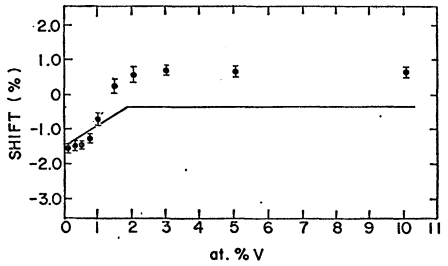

FIG. 16. The V^{51} Knight shift for AuV from the work of Narath, Gossard, and Wernick (Ref. 49). The solid lines are theoretical estimates based on the analysis of Sec. V.

Fig. 16):

(i) The Knight shift extrapolated to zero V concentration is $K=-1.5\%$. On the other hand, from the known susceptibility, one would estimate[49] a negative Knight shift of approximately -5% assuming one-half of the susceptibility arises from the V $3d$ shell. Thus there appears to be an extra positive contribution of order $+4\%$.

(ii) The Knight shift increases with vanadium concentration up to about 2% V, at which point it becomes concentration-independent.

Contributions of the kind needed to explain both (i) and (ii) above are to be expected from the $A(r)$ polarization term of Eq. (43). In the limit of very low concentrations at a given V site only $A(0)$, i.e., the polarization from that particular site, is significant. This gives a positive contribution to the Knight shift of the correct magnitude as shown below. As the V concentration is increased, the long-range polarization for the other V impurities becomes increasingly important. This, also, has the correct magnitude and the proper behavior with increasing concentration.

Let us first of all estimate the zero concentration contribution. From Appendix B, Eq. (B2),

$$A(0)=|\sum_k p_{0k}|^2$$

$$=2kT_KN(0)[\ln(D/kT_K)]^2. \quad (49)$$

Thus

$$\sigma(0)=\langle S_z\rangle N(kT_K/E_F)[\ln(D/kT_K)]^2. \quad (50)$$

From the susceptibility[17] one estimates $|\langle S_z\rangle|\simeq 2\times10^{-3}$ in a 10-kG field. (Assuming one-half of the measured χ comes from the V d spins.) Therefore, this contribution to the Knight shift is

$$\Delta K_0=(A_N/g_N\mu_N)10^{-6}(kT_K/5E_F)[\ln(D/kT_K)]^2. \quad (51)$$

Assuming $A_N/g_N\mu_N\simeq3\times10^6$ Oe, $kT_K\simeq300$°K, $E_F\simeq5.5$ eV, and a cutoff of approximately d-band width (2 eV), we obtain

$$\Delta K_0\simeq+5\%.$$

The result is of the right magnitude as discussed in (i) above.

As the vanadium concentration is increased the long-range polarization resulting from the other V sites becomes significant. We estimate this concentration-dependent excess shift in the manner described above for CuFe. From Appendix B, Eq. (B12), we obtain for AuV

$$A(r)\simeq20N(kT_K/E_F)((\sin k_Fr)/k_Fr)^2, \quad (52)$$

from which we obtain for the excess shift

$$\Delta K\simeq\pi cN\times10^{-17}\left(\frac{\xi}{\lambda}\right). \quad (53)$$

In obtaining the above we have used $E_F\simeq5.5$ eV, $T_K\simeq300$°K, and assumed $\langle S_z\rangle\simeq2\times10^{-3}$ in a 10-kG field as in the $A(0)$ estimate. Again the smaller of the lengths ξ or λ is to be used in Eq. (53), depending on the conditions. The mean free path may be estimated from the residual resistivity[17] (15 $\mu\Omega$ cm/at.%V) using a free-electron model as

$$\lambda\simeq50\times10^{-8}/c \text{ cm}. \quad (54)$$

At low concentrations, where $\lambda\gg\xi$, we expect the Knight shift to increase linearly with concentration. However, above roughly 2% the mean-free-path limits the quasiparticle wave function and one expects concentration-independent behavior. From the data of Fig. 16, the crossover concentration is $c\simeq1.8\%$, at which point $\lambda\sim30$ Å. This is to be compared with the estimated value of $\xi_0\simeq100$ to 200 Å. Note that in both the CuFe and AuV, one can improve the agreement with experiment by assuming the effective experimental coherence length is of order $\frac{1}{5}\xi_0$. Above the crossover concentration Eqs. (53) and (54) predict an excess shift of approximately $+1.1\%$, as shown in Fig. 16. Once again the estimated shift has the correct magnitude. In addition, the agreement between the turnover point and the calculated concentration where $\lambda\sim\xi$ is gratifying. However, we point out that the data indicate a nonlinear initial behavior. A probable explanation of this nonlinearity lies in the fact that the treatment of the Au lattice as a continuous homogeneous solid is seriously in error in the case of nearest- and next-nearest-neighbor impurities. (A single nearest-neighbor impurity produces approximately a 0.3% shift in AuV according to the above estimates.) A more precise calculation should explicitly sum over lattice sites in order to take such details properly into account.

The long-range quasiparticle polarization provides a natural explanation of the abrupt change in behavior of the V^{51} Knight shift in the 1% concentration range

where no anomalies are observed in any of the macroscopic properties.[17] On the basis of this interpretation, the *Au*V data of Fig. 16 provide the first indirect measurement of the coherence length in the magnetic impurity problem.

VI. CONCLUSION

The experimental results presented and summarized in this paper strongly support the existence of a spin-compensated ground state for the magnetic impurity problem. In particular, the specific-heat data, NMR linewidths, and excess Knight shifts suggest that the AK many-body singlet provides the essential features of the ground-state and low-temperature properties of such a system. More experimental data is needed; especially in connection with the long-range conduction-electron spin polarization associated with the quasiparticle.

We note, finally, that the *Au*V data as interpreted in this paper can be understood in terms of the Kondo effect at concentrations at least as high as 10% V. On the other hand, it has recently been shown that the ordered alloy Au_4V (20% V) is ferromagnetic.[50] It may indeed be the case that these seemingly diverse phenomena are related and that the study of the magnetic impurity problem will lead us directly to a better understanding of magnetism in transition metals.

Note added in proof. The proportionality between the linewidth and the total susceptibility established by Fig. 7, although correct, may not be the proper way of looking at the result. In fact, to establish that only RKKY polarization contributes to the linewidth one should plot linewidth versus *local* susceptibility. This point is being pursued.

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[50] L. Creveling, H. L. Luo, and G. S. Knapp, Phys. Rev. Letters **18**, 851 (1967).

APPENDIX A: EVALUATION OF THE COMMUTATORS

Straightforward computation of Θ_{kq} and S_z using Eqs. (1), (2), and (5) yields

$$i\dot{\Theta}_{kq}=\sum_{lm}p_{l\,k+q}p_{mk}(\lambda_m-\lambda_l)[a_{l\uparrow}{}^{\dagger}a_{m\uparrow}-a_{l\downarrow}{}^{\dagger}a_{m\downarrow}]$$
$$+(J/N)f_0{}^2\sum_l\{p_{l\,k+q}p_{0k}[(a_{l\uparrow}{}^{\dagger}a_{0\uparrow}+a_{l\downarrow}{}^{\dagger}a_{0\downarrow})S_z$$
$$+a_{l\uparrow}{}^{\dagger}a_{0\downarrow}S^-\!-a_{l\downarrow}{}^{\dagger}a_{0\uparrow}S^+]\!-p_{0\,k+q}p_{lk}[(a_{0\uparrow}{}^{\dagger}a_{l\uparrow}$$
$$+a_{0\downarrow}{}^{\dagger}a_{l\downarrow})S_z\!-a_{0\uparrow}{}^{\dagger}a_{l\downarrow}S^-\!+a_{0\downarrow}{}^{\dagger}a_{l\uparrow}S^+]\}+\tfrac{1}{2}g\mu_B$$
$$\times\sum_{\mathbf{p}}H(\mathbf{p})[(C_{\mathbf{k+q}\uparrow}{}^{\dagger}C_{\mathbf{k-p}\uparrow}+C_{\mathbf{k+q}\downarrow}{}^{\dagger}C_{\mathbf{k-p}\downarrow})$$
$$-(C_{\mathbf{k+q+p}\uparrow}{}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\mathbf{k+q+p}\downarrow}{}^{\dagger}C_{\mathbf{k}\downarrow})], \quad \text{(A1)}$$
$$i\dot{S}_z=(J/N)f_0{}^2[a_{0\downarrow}{}^{\dagger}a_{0\uparrow}S^+-a_{0\uparrow}{}^{\dagger}a_{0\downarrow}S^-]. \quad \text{(A2)}$$

We will calculate only the first-order effects of the magnetic field and so we now discard all terms of higher order. In Eqs. (A1) and (A2) we can drop all terms with $l\neq 0$ in the interaction part (J) since in the ground state there is no mixing of these operators and hence terms containing them are of higher order than H. We rewrite the C operator in the field term $H(p)$ in terms of the a operators and again drop the off-diagonal parts, giving

$$i\dot{\Theta}_{kq}=\sum_{lm}p_{l\,k+q}p_{mk}(\lambda_m-\lambda_l)(a_{l\uparrow}{}^{\dagger}a_{m\uparrow}-a_{l\downarrow}{}^{\dagger}a_{m\downarrow})$$
$$+2(J/N)f_0{}^2p_{0\,k+q}p_{0k}(a_{0\uparrow}{}^{\dagger}a_{0\downarrow}S^-\!-a_{0\downarrow}{}^{\dagger}a_{0\uparrow}S^+)$$
$$+\tfrac{1}{2}g\mu_BH(q)(n_{k+q}{}'-n_k')+\tfrac{1}{2}g\mu_B\sum_{\mathbf{p}}H(p)(p_{0\,k+q}p_{0\,k-p}$$
$$-p_{0\,k+q+p}p_{0k})(a_{0\uparrow}{}^{\dagger}a_{0\uparrow}+a_{0\downarrow}{}^{\dagger}a_{0\downarrow}) \quad \text{(A3)}$$

and

$$i\dot{S}_z=(J/N)f_0{}^2(a_{0\downarrow}{}^{\dagger}a_{0\uparrow}S^+-a_{0\uparrow}{}^{\dagger}a_{0\downarrow}S^-). \quad \text{(A4)}$$

In Eq. (A3), the operators $n_{k+q}{}'$ and n_k' are obtained from terms of the form

$$p_{l\,k+q}p_{m\,k-p}(a_{l\uparrow}{}^{\dagger}a_{m\uparrow}+a_{l\downarrow}{}^{\dagger}a_{m\downarrow}).$$

Since only $l=m$ terms are lowest order and $p_{l\,k+q}p_{l\,k-p}$ is sharply peaked about $k+q=k-p$,

$$n_{k+q}{}'=\sum_{l\neq 0}p_{l\,k+q}p_{l\,k+q}(a_{l\uparrow}{}^{\dagger}a_{l\uparrow}+a_{l\downarrow}{}^{\dagger}a_{l\downarrow}). \quad \text{(A5)}$$

APPENDIX B: EVALUATION OF THE RANGE FUNCTION $A(r)$

From Eq. (20) of the text

$$A(r)=\sum_{kk'}p_{0k}p_{0k'}\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}] \quad \text{(B1)}$$
$$=|\sum_k p_{0k}\exp(i\mathbf{k}\cdot\mathbf{r})|^2. \quad \text{(B2)}$$

Using the definition of p_{0k} and taking $\epsilon_k=\hbar^2k^2/2m$,

$$A(r)=\frac{kT_K}{2N(0)}\frac{1}{(2\pi)^4}\left|\int_0^{k_{\max}}\frac{k^2dk}{|\epsilon_F-\epsilon_k|+\epsilon_B}\times\int_{-1}^{1}\exp(ikr\cos\theta)\,d(\cos\theta)\right|^2. \quad \text{(B3)}$$

This may be put simply into the form

$$A(r)=\tfrac{9}{16}N(kT_K/E_F)[\,|I(r)|^2/(k_Fr)^2], \quad \text{(B4)}$$

where the integral $I(r)$ is defined

$$I(r)=\int_0^{E_F}\frac{\sin[(2m\epsilon/\hbar^2)^{1/2}r]d\epsilon}{|E_F-\epsilon|+\epsilon_B}. \quad \text{(B5)}$$

Since $|I(r)|^2$ is clearly positive definite, the function $A(r)$ is of a fixed sign and falls off as r^{-2}. As a result, impurities far from a given lattice site contribute to the spin polarization at that site. In fact, the characteristic distance r_c of maximum contribution is of order the coherence length or the mean free path, whichever is shorter (see discussion in Sec. V). For *Cu*Fe we take r_c to be typically 500 to 1000 Å. In evaluating $I(r)$ one can take the factor $\sin k_Fr$ outside the integral provided the range of integration is restricted to energies such that $\Delta kr_c<1$, where Δk is defined by

$$|E_F-\epsilon|\simeq 2E_F(\Delta k/k_F). \quad \text{(B6)}$$

For larger values of Δk the sine factor oscillates rapidly in the region of spatial interest, giving no net contribution. Thus

$$|E_F-\epsilon|<2E_F(1/k_Fr_c)\sim 5\times10^{-3}E_F \quad \text{(B7)}$$

for *Cu*Fe. Thus

$$|I(r)|^2=(\sin k_Fr)^2[\ln(5\times10^{-3}E_F/\epsilon_B)]^2 \quad \text{(B8)}$$

$$\simeq 5(\sin k_Fr)^2. \quad \text{(B9)}$$

Thus we estimate, for *Cu*Fe,

$$A(r)\simeq 3N(kT_K/E_F)\,((\sin k_Fr)/k_Fr)^2. \quad \text{(B10)}$$

This result is of the same form as that obtained for the spin-correlation function by Nagaoka.[9]

We can check the above estimate for $I(r)$ by noting the normalization condition

$$\int_0^{\xi}A(r)\,d^3r\simeq 1, \quad \text{(B11)}$$

where ξ is the coherence length $\hbar v_F/kT_K\simeq 5\times10^{-5}$ for *Cu*Fe. Using the values $kT_K\simeq 15$°K and $E_F=7$ eV for *Cu*Fe one obtains from Eq. (B11)

$$\xi\simeq 5\times10^{-5}.$$

The result is consistent with the estimated coherence length. Thus the above numerical estimate for $|I(r)|^2$ gives the proper normalization.

A similar estimate can be made for any system where T_K is known. For *Au*V the situation is somewhat simpler. Because of the large value of T_K, one can integrate Eq. (B5) all the way to E_F, giving for *Au*V

$$A(r)\simeq 20N(kT_K/E_F)\,((\sin k_Fr)/k_Fr)^2. \quad \text{(B12)}$$

Again the normalization condition can be used as a check. The resulting value $\xi\sim 50$ Å is in agreement with the experimentally inferred value (see Sec. V).

APPENDIX C: DEVELOPMENT OF CONDUCTION-ELECTRON SUSCEPTIBILITY EQUATION

In this Appendix we give the details leading from Eqs. (18) to (36). Consider the quantity

$$\Gamma_{kq}=\sum_{ll'}p_{l\,k+q}p_{l'k}(\lambda_{l'}-\lambda_l)[a_{l\uparrow}{}^\dagger a_{l'\uparrow}-a_{l\downarrow}{}^\dagger a_{l'\downarrow}]$$

$$=\sum_{ll',k_1k_2}p_{l\,k+q}p_{l'k}p_{lk_1}p_{l'k_2}(\lambda_{l'}-\lambda_l)\times(C_{k_1\uparrow}{}^\dagger C_{k_2\uparrow}-C_{k_1\downarrow}{}^\dagger C_{k_2\downarrow}). \quad \text{(C1)}$$

Now

$$\sum_{ll',k_1k_2}p_{l\,k+q}p_{l'k}p_{lk_1}p_{l'k_2}\lambda_{l'}=\sum_{l',k_1k_2}\delta_{k_1,k+q}p_{l'k}p_{l'k_2}\lambda_{l'}, \quad \text{(C2)}$$

$$\sum_{ll',k_1k_2}p_{l\,k+q}p_{l'k}p_{lk_1}p_{l'k_2}\lambda_{l}=\sum_{l,k_1k_2}\delta_{k_2,k}p_{l\,k+q}p_{lk_1}\lambda_{l}. \quad \text{(C3)}$$

Thus

$$\Gamma_{kq}=\sum_{lk_1}p_{lk}p_{lk_1}\lambda_l(C_{k+q\uparrow}{}^\dagger C_{k_1\uparrow}-C_{k+q\downarrow}{}^\dagger C_{k_1\downarrow})-\sum_{lk_1}p_{l\,k+q}p_{lk_1}\lambda_l(C_{k_1\uparrow}{}^\dagger C_{k\uparrow}-C_{k_1\downarrow}{}^\dagger C_{k\downarrow}). \quad \text{(C4)}$$

Using the identity

$$\sum_{lk_1}p_{lk}p_{lk_1}\lambda_l=\sum_{lk_1}p_{lk}p_{lk_1}(\epsilon_{k_1}+\lambda_l-\epsilon_{k_1})=\sum_{k_1}\epsilon_{k_1}\delta_{k,k_1}+\sum_{lk_1}(\lambda_l-\epsilon_{k_1})p_{lk}p_{lk_1}, \quad \text{(C5)}$$

we write

$$\Gamma_{kq}=(\epsilon_k-\epsilon_{k+q})[C_{k+q\uparrow}{}^\dagger C_{k\uparrow}-C_{k+q\downarrow}{}^\dagger C_{k\downarrow}]+\sum_{lk_1}p_{lk}p_{lk_1}(\lambda_l-\epsilon_{k_1})[C_{k+q\uparrow}{}^\dagger C_{k_1\uparrow}-C_{k+q\downarrow}{}^\dagger C_{k_1\downarrow}]-\sum_{lk_1}p_{l\,k+q}p_{lk_1}(\lambda_l-\epsilon_{k_1})[C_{k_1\uparrow}{}^\dagger C_{k\uparrow}-C_{k_1\downarrow}{}^\dagger C_{k\downarrow}]. \quad \text{(C6)}$$

From AK we have

$$(\lambda_l-\epsilon_{k_1})\,p_{lk_1}=-\tfrac{1}{2}\mu_l p_{0k_1}.$$

Thus

$$\Gamma_{kq}=(\epsilon_k-\epsilon_{k+q})\Theta_{kq}-\sum_{lk_1}\tfrac{1}{2}\mu_l p_{lk}p_{0k_1}(C_{k+q\uparrow}{}^\dagger C_{k_1\uparrow}-C_{k+q\downarrow}{}^\dagger C_{k_1\downarrow})+\sum_{lk_1}\tfrac{1}{2}\mu_l p_{l\,k+q}p_{0k_1}(C_{k_1\uparrow}{}^\dagger C_{k\uparrow}-C_{k_1\downarrow}{}^\dagger C_{k\downarrow}). \quad \text{(C7)}$$

Using Eq. (53) from AK we have

$$\sum_l \tfrac{1}{2}\mu_l p_{lk} = \sum_{lk} \epsilon_k p_{0k} p_{lk} p_{lK} = \sum_K \epsilon_K p_{0K} \delta_{kK} = \epsilon_k p_{0k}. \quad \text{(C8)}$$

Thus

$$\Gamma_{kq} = (\epsilon_k - \epsilon_{k+q})\Theta_{kq} - \sum_{k_1} \epsilon_k p_{0k} p_{0k_1} (C_{k+q\uparrow}{}^\dagger C_{k_1\uparrow} - C_{k+q\downarrow}{}^\dagger C_{k_1\downarrow}) + \sum_{k_1} \epsilon_{k+q} p_{0\,k+q} p_{0k_1} (C_{k_1\uparrow}{}^\dagger C_{k\uparrow} - C_{k_1\downarrow}{}^\dagger C_{k\downarrow}). \quad \text{(C9)}$$

Transforming back to the scattering-state representation,

$$\Gamma_{kq} = (\epsilon_k - \epsilon_{k+q})\Theta_{kq} - \epsilon_k p_{0k} \sum_l p_{l\,k+q} (a_{l\uparrow}{}^\dagger a_{0\uparrow} - a_{l\downarrow}{}^\dagger a_{0\downarrow}) + \epsilon_{k+q} p_{0\,k+q} \sum_l p_{lk} (a_{0\uparrow}{}^\dagger a_{l\uparrow} - a_{0\downarrow}{}^\dagger a_{l\downarrow}). \quad \text{(C10)}$$

Taking averages in the perturbed state

$$\langle \Gamma_{kq} \rangle = (\epsilon_k - \epsilon_{k+q}) \langle \Theta_{kq} \rangle + (\epsilon_{k+q} - \epsilon_k) p_{0k} p_{0\,k+q} \times \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow} \rangle. \quad \text{(C11)}$$

Inserting this into Eq. (18) yields Eq. (36). In the final step we have used the result

$$\langle a_{l\uparrow}{}^\dagger a_{0\uparrow} - a_{l\downarrow}{}^\dagger a_{0\downarrow} \rangle = \langle a_{0\uparrow}{}^\dagger a_{0\uparrow} - a_{0\downarrow}{}^\dagger a_{0\downarrow} \rangle \delta_{l0}, \quad \text{(C12)}$$

which may be proven quite simply from consideration of the equation of motion of the operator.

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Influence of Radio-Frequency Magnetic Fields on the Mössbauer Effect in Magnetic Co^{57} Sources*

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Experiments are described that demonstrate the destruction of the Mössbauer hyperfine pattern by the action of a radio-frequency magnetic field. Two possible mechanisms for the effect are considered: magnetostriction and domain-wall passage. Calculations make magnetostriction seem unlikely, leaving as the probable cause the fluctuations in the γ-ray energy resulting from the alteration in the direction of the hyperfine field after the passage of a domain wall. This is calculated with the aid of the theory of motional narrowing in NMR and a demonstration by Peshkin of the correspondence between the γ ray and the NMR case. The hypothesis of 180° walls is found to be inadequate, and a less restrictive assumption is needed.

INTRODUCTION

A REPORT[1] at the Allerton House Conference on the Mössbauer effect described a magnetic-resonance method of measuring the g factor of the 14.4-keV excited state of Fe^{57} in iron metal. The technique was to apply a steady field of a few hundred oersteds parallel to the plane of a foil and a rf magnetic field of a few oersteds also in the plane but perpendicular to the dc field. A change in the transmission of the radiation from a Co^{57} source in an iron lattice was sought for at the frequency of 26 MHz, which corresponds to the separation between successive hyperfine levels of the excited nuclear state. The possibility of such an effect arises from the fact that the hyperfine field of 330 kOe lies parallel to the atomic moment, and thus even quite weak external rf fields, by changing the direction of the magnetization, cause directional changes in the hyperfine field and hence equivalent large hyperfine rf fields. Theory shows[2] that such fields produce a resonant line splitting, equivalent to a frequency modulation of the γ-ray line. This would result in an increase in transmission. Such an effect was apparently seen, but an obscuring nonresonant effect resulted in a large change in transmission between rf on and rf off, at frequencies well away from 26 MHz. The present work arose in part in an effort to understand this phenomenon.

An additional aim in starting the research was to attempt to perform a series of simple experiments in γ-ray optics similar in principle to the sort of optical experiments discussed by Righi.[3] For example, if the linearly polarized radiation emerging perpendicular to

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[1] G. J. Perlow, University of Illinois, Allerton Park Conference Report, 1960 (unpublished). This talk presents work done by E. C. Avery, C. Littlejohn, G. J. Perlow, and B. Smaller. A more recent experiment showing the resonance by rf means is reported by E. Matthias, University of California, Lawrence Radiation Laboratory Report No. UCRL-17877 (unpublished).

[2] M. N. Hack and M. Hamermesh, Nuovo Cimento 19, 546 (1961).