δ is of order 50 G,[10] so that $\delta/\omega_0 \cong 0.02$ and the adiabatic cancellation of the Yosida shift is effective.[12]

We have not extended Eq. (12) to include the second-order Kondo-type shift of Eq. (9), but use the first-order results to give a qualitative discussion of the effects of spin-lattice coupling on this shift. The second-order shift results from spontaneous fluctuations of the conduction-electron magnetization about the mean instantaneous spin direction. We now propose that adiabatic following of this second-order shift is much more easily suppressed by spin-lattice coupling than is the first-order shift. Qualitatively we would expect Δ of order $J\rho(\epsilon_F) \times [2J\langle S^z\rangle(N_i/N)]\{1+\ln(\gamma\beta D/\pi)\}$, i.e., δ/ω_0 of order $[J\rho(\epsilon_F)]^2[1+\ln(\gamma\beta D/\pi)]$ to suppress cancellation of the second-order shift. In the temperature range above 10°K for the 1.5% alloy we would therefore expect the second-order shift to be experimentally observable despite the absence of the first-order shift.

We conclude that in view of the considerable interest in the nature of the Kondo screening cloud (the present calculations are not to high enough order in J to include the possibility of a Nagaoka-type bound state) it would be worthwhile trying to observe its properties via the temperature dependence of the local-moment spin-resonance frequency in dilute transition-metal alloys.

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EVIDENCE FOR A SINGLET GROUND STATE IN THE MAGNETIC IMPURITY PROBLEM*

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Nuclear-magnetic-resonance studies on dilute alloys of Fe in Cu metal give evidence for the existence of a singlet ground state for the magnetic impurity problem. The moment on the impurity is found to increase linearly with magnetic field but is independent of temperature in the region $kT \ll \mu_B H \ll kT_K$.

Since Kondo[1] showed that the amplitude for scattering of the conduction electrons by a magnetic impurity diverges logarithmically with decreasing temperature, there has been intensive interest in the behavior of the conduction electron–magnetic impurity system near absolute zero. A number of authors[2] suggested that there would be a reduction of the magnetic moment on the impurity as a result of spin correlations with the conduction electrons. In fact it has recently been shown[3] that at zero temperature the system is unstable with respect to the formation of a many-body singlet state. Although there have been a variety of experimental studies[4] carried out which indicate an apparent reduction in the impurity moment at low temperature, the magnetic character of the ground state has remained unsettled. In this Letter we present the results of an experimental investigation of the low-temperature magnetic properties of dilute Fe impurities in Cu metal using nuclear-magnetic-resonance techniques. The results are in agreement with the behavior expected of a conduction electron–impurity singlet state.

It is well known that a localized magnetic perturbation in a metal produces Ruderman-Kittel-Kasuya-Yosida (RKKY)[5] spin-density oscillations in the conduction electrons. These oscillations are due to the presence of a sharp Fermi surface and arise whenever the conduction-electron scattering from an impurity is spin dependent. For a singlet state the scattering is not spin dependent (both orientations of the impurity spin are coherently mixed) and no RKKY oscillations will occur.[6] However, if the impurity contribution to the susceptibility is finite, the application of a magnetic field will result in spin-dependent scattering proportional to the magnetic field. Since in the correlated state the Fermi surface remains essentially sharp ($\Delta k/k_F \sim 10^{-4}$), whatever local magnetic moment is induced by the magnetic field will result in well-defined time-averaged spin-density oscillations in the vicinity of an impurity.[7] We expect these oscillations to be of the RKKY form, but the detailed spatial dependence awaits a solution in a finite magnetic field. Such oscillations can be observed by a study of the nmr linewidths on the host nuclei[8] since nearby nuclei probe the spin-density oscillations via the hyperfine interaction. Therefore one can use the Cu nuclear magnetic resonance in Cu:Fe to measure the magnitude and field dependence of the impurity moment.

The apparatus involves standard paramagnetic-salt demagnetization techniques. We are able to obtain temperatures down to 0.02°K with experimental running time at the lowest temperatures of approximately $1\frac{1}{2}$ h. Thermal contact from the sample to the cooling salt is made by Ag wires. The sample consists of a mixture of Cu:Fe powder (~30 μ particle size) and Al powder attached to the silver wires with epoxy and surrounded by a low-frequency silver nmr coil. The nmr absorption signal is measured with a standard low-level Robinson oscillator employing frequency modulation. The resonance is done in a high-homogeneity Varian magnet. The sample temperature is measured by recording the amplitude of the Al nmr signal (Curie law) which is calibrated at higher temperatures against the He^4 vapor-pressure temperature scale. The two Cu:Fe samples used in these experiments were prepared from high-purity copper by arc melting and contained 0.076 and 0.013 at.% Fe by analysis. Metallographic study revealed no precipitation on the grain boundaries, and the resistivity ratio (2.65 for the more concentrated sample) agreed well with the known residual resistivity of Fe in Cu[9] (~10 $\mu\Omega$ cm/at.%).

The experimental results for the 0.076-at.% Fe in Cu sample are shown in Fig. 1. The Cu^{63} linewidth is seen to increase linearly with field in the range investigated where $kT \ll \mu_B H \ll kT_K$. The linewidths are independent of temperature from 0.02 to 0.5°K above which the signal-to-noise ratio in the present system makes accurate measurements difficult. The higher temperature work of Sugarawa[8] on Cu:Fe indicates that the Cu^{63} linewidth for the 0.076-at.% concentration of our sample will be 120 G when fully saturated. The dashed curve of Fig. 1 is the initial slope of a spin-2 Brillouin function (for $T = 0.02$°K) which saturates at the 120-G value. Thus we see that at the lowest temperatures in question thermal fluctuations of the moment are eliminated well below 1 kG and the observed linear increase in linewidth with applied field indicates a corresponding increase in the time-average magnitude of the moment on the impurity. The results show that in a 2-kG magnetic field at these temperatures the

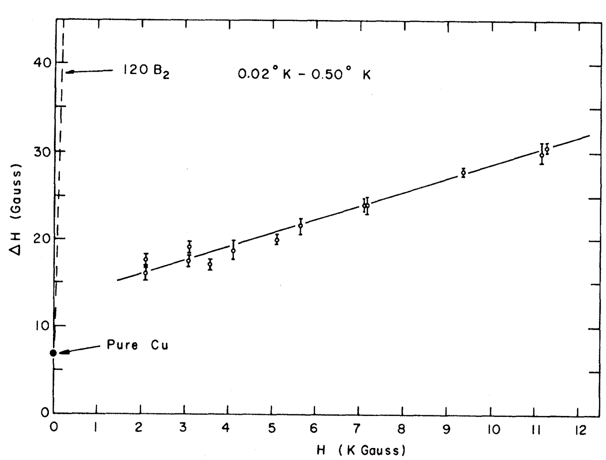

FIG. 1. Peak-to-peak nmr linewidths for Cu^{63} in Cu $+0.076$ at.% Fe. The dashed line is the initial slope of a spin-2 Brillouin function which saturates at 120 G.

time-averaged impurity moment is more than an order of magnitude smaller than the saturated value.

In zero magnetic field (and at $T = 0°K$), the singlet state is formed from pairing correlations between the impurity spin and the conduction electrons within a coherence distance ξ ($\cong \hbar v_F / kT_K$) about the impurity.[2,3] Because of the quantum mechanical nature of a singlet state the time-average moment on the impurity will be 0. However, when a magnetic field is applied one might expect the singlet pairing to be reduced in order to make use of Zeeman energy. Recent calculations in finite field[10] confirm this expectation and give for the low-temperature susceptibility ($kT \ll kT_K$)

$$\chi(0) \propto \mu_B^2 / kT_K, \quad (1)$$

where μ_B is the Bohr magneton and kT_K is the condensation energy at 0°K.[3] As a result of the finite susceptibility, the magnetic moment should increase linearly with field but not attain its full value until $\mu_B H \cong kT_K$.

The linearity and slope of the dependence of linewidth on magnetic field are in agreement with Eq. (1) if one takes T_K from the maximum in the specific-heat data of Franck, Manchester, and Martin.[11] These results show a large anomaly in the specific heat which occurs at about 5°K independent of concentration. The area under the anomaly is consistent with complete removal of the spin entropy of the impurity moment as expected for a singlet ground state. Thus the value of T_K for Cu:Fe is found from both the nmr and specific-heat data to be about 5°K. This is consistent with the data of White[12] and Daybell and Steyert[4] in which the resistivity is found to approach saturation below this temperature. The 15°K value of T_K estimated by Daybell and Steyert is probably too large as a result of fitting to Nagaoka's theory at high temperatures where it is inaccurate. Furthermore, since the resistivity cannot increase beyond the unitarity limit, the effect of the large residual resistivity due to resonant scattering in Cu:Fe must be taken into account.

The data for the more dilute sample (0.013-at.% Fe) show a field-dependent excess linewidth of a magnitude and slope consistent with the reduced concentration. For this sample the extrapolation to zero field gives the pure Cu^{63} linewidth of 6.4 ± 0.2 G, whereas the extrapolation in Fig. 1 to zero field gives an intercept of approximately 13 G. The fact that the zero-field extrapolated linewidth shows some broadening at the higher concentration may be accounted for as the result of quenching of the singlet state when two Fe impurities are sufficiently close ($\lesssim 2$ lattice constants) that the internal exchange fields are greater than kT_K. Quadrupolar effects due to the Fe impurities also contribute some residual linewidth. Thus the small residual width is probably not significant, but further study is in order.

One might be tempted to explain the anomalous field dependence on the basis of short-range magnetic ordering.[13] This is not the case for although the bulk magnetization would show anomalous saturation behavior, the expectation value of the moment along the local axis of quantization would be the total moment and so the full RKKY spin-density oscillations would be present. We have verified that this is the case by measurements on a Cu:Mn sample where a field-independent linewidth of precisely the value expected from high-temperature data is seen even though short-range order is known to be present at these concentrations (0.03 at.%) and temperatures ($T < 0.1°K$), so that the bulk magnetization does not saturate even for $\mu_B H / kT \gg 1$.[14] Also, crystal-field effects could in principle lead to a nondegenerate ground state, but this is not likely for Cu:Fe for two important reasons. Firstly, Anderson[15] has shown that the quenching of the orbital moments for iron-group solutes results from the covalent s-d admixture in which case the crystal-field effects are unimportant. Secondly, even in an insulator the Fe^{2+} configuration in an octahedral coordination has a degenerate ground state.

The above experimental results provide additional evidence for the existence of a nonmagnetic ground state for the "magnetic impurity problem." The other available data on the Cu:Fe system are consistent with this picture.[16] However, there is not yet any experimental information on the long-range spin coherence of the conduction electrons near the impurity expected for the singlet ground state.[2,3]

Finally, we wish to mention preliminary measurements of the Cu^{63} spin-lattice relaxation time T_1 in this system. One finds for the sample of Fig. 1 that below T_K, the product T_1T falls rapidly to about 0.7 of the value for pure copper and then remains essentially temperature independent. Such measurements promise to give detailed information on the conduction-electron spin-flip correlation time in the ground state and will be considered in detail in a subsequent publication.

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RELAXATION AND RECOMBINATION TIMES OF QUASIPARTICLES IN SUPERCONDUCTING Al THIN FILMS

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Recently[1] there has been considerable interest in the decay of excited quasiparticles in superconductors. It has been conjectured[1] that an excited quasiparticle of energy E decays via a two-step process. The first consists of a relaxation in time τ_T to energy Δ, where 2Δ is the energy gap of the superconductor. This process occurs primarily by emission of a phonon of energy $E-\Delta$.[2,3] The second step is recombination in time τ_R of two quasiparticles at energy Δ to form a Cooper pair and is accompanied by the emission of a phonon of energy 2Δ.[4,5]

We have measured for the first time τ_T in thin aluminum films at 0.37°K and find that τ_T decreases exponentially as a function of $(E-\Delta)/\Delta$ and is $\sim 0.5\times10^{-8}$ sec at $(E-\Delta)/\Delta = 1.0$. We have also measured τ_R as a function of temperature and find that at 0.37°K, $\tau_R \sim 1.0 \times 10^{-6}$ sec and that it decreases with increasing temperature up to $T\sim 1.2$°K. At temperatures above 1.2°K,[6] τ_R appears to increase