Measurements of electron-spin density near Co atoms in Cu†

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We report nuclear-magnetic-resonance studies of *Cu* Co in which we resolve and identify satellites due to three shells of Cu near neighbors around isolated Co impurities. The satellite positions show that the spatial form of the spin polarization oscillates with distance and that the conduction electrons on these atoms contribute about -8% of the total impurity susceptibility. The splittings are measured from 1.5 to 450 °K and from 6.4 to 63 kG and compared with the susceptibility χ of singles. The width of the main line is decomposed into contributions Δ_1 and Δ_2 from isolated Co atoms and pairs of Co atoms, respectively, by use of the temperature variation of the splitting and of the pair susceptibility χ_2. The theory of Walstedt and Walker is used to show that Δ_1 agrees with what one would expect from the satellite splittings, and that Δ_1/Δ_2 is reasonable in terms of the magnitude and temperature dependence of χ_1 and χ_2. The results are scaled to *Cu*Fe to show that much of the observed linewidth anomaly is of the same origin, and must be included before possible conclusions can be made about Kondo correlation effects.

I. INTRODUCTION

The detailed understanding of how an isolated magnetic atom behaves when dissolved in a nonmagnetic metal, of the circumstances under which it possesses a permanent moment, has long been an area of interest.[1-7] An important subclass of problems is concerned with the Kondo effect, which may be characterized as the apparent change from the temperature-independent susceptibility at low temperatures characteristic of an atom lacking a permanent moment to a near Curie-law behavior at high temperature characteristic of an atom possessing a permanent moment.

A variety of theoretical approaches have been employed[2] but they broadly follow one of two models. One, the s-d exchange model, starts with an atom that possesses a permanent moment. This model describes the disappearance of the permanent moment at low temperature resulting from the s-d exchange coupling to the electrons. The other, the localized-spin-fluctuation (LSF) model,[5] starts with the nonmagnetic limit of the Anderson-Wolff-Friedel model,[2] and describes the appearance of the permanent moment at high temperatures. The temperature which roughly divides high-temperature from low-temperature experimental behavior is called the Kondo temperature T_K, its exact definition depending on the detailed theory as well as the physical property being computed.

Much effort has been devoted to determining which of these models gives a better description of the various physical systems.[7,8] Unfortunately, direct comparison between predictions of the two models has been hampered by difficulties in obtaining results based on exact solutions of the problem. For example, calculations of the spatial form and extent of the conduction-electron-spin density $\sigma(\vec{r})$ for temperatures below the Kondo temperature have given rather different results depending on the model and/or approximations used.[2,7,9,10] Calculations based on the s-d Hamiltonian give the well-known Ruderman-Kittel-Kasuya-Yosida (RKKY) form for $T > T_K$, but for $T < T_K$ there is no general agreement as to the correct form of $\sigma(\vec{r})$.

Nagaoka predicted the ground state was a many-body singlet with an extended spatial range of the order $\xi \sim (E_F/k_B T_K k_F)$,[11] where E_F is the Fermi energy, k_B is Boltzmann's constant, and k_F is the wave vector of electrons at the Fermi surface. Using a calculation based on the Kondo-Applebaum ground state, Heeger predicted the formation of a spatially extended spin polarization for $T < T_K$, which accounted for half of the total impurity contribution to the magnetic susceptibility.[7] Bloomfield, Hecht, and Sievert, on the other hand, used two-time thermodynamic Green's functions to show that the s-d model predicts no long-range nonoscillatory components to the spin density, and that the susceptibility contributed by the conduction electrons is an order of magnitude less than that localized at the impurity and is aligned antiferromagnetically.[11] Other calculations, based on different approximate solutions of the Kondo model, have yielded somewhat different results.[2,7,11] Golibersuch and Heeger reported the experimental observation of an extended spin polarization in *Cu*Fe from measurements of the Cu NMR linewidth.[7,12] Potts and Welsh later extended these studies.[13] Stassis and Shull subsequently studied *Cu*Fe using neutron diffraction and reported no such extended spin polarization.[14] The current status has been reviewed by Narath.[3]

The classic Kondo system for copper based alloys is *Cu*Fe. The question naturally arises: is *Cu*Co a Kondo system? Daybell and Steyert point out that studies of susceptibility, resistivity, specific heat, and thermopower indicate a behavior

qualitatively similar to *Cu*Fe ($T_K \cong 30$ °K) but with $T_K \sim 1000$ °K.

Ordinarily *Cu*Fe is said to be magnetic in Anderson's sense,[2] *Cu*Ni nonmagnetic, and *Cu*Co on the borderline, a reasonable result since Co is the atom between Fe and Ni in the periodic table. For example, when dissolved in copper, Co atoms have a magnetic susceptibility 17 times larger than Ni. These facts lead us to believe that the *Cu*Co results have in all likelihood substantial elements in common with *Cu*Fe, and thus should be examined for bearing on theories of the Kondo effect.

In this paper we report the NMR measurement of $\sigma(\vec{r})$ in the vicinity of Co atoms dissolved in a Cu host for $T \ll T_K$. A preliminary account of this work has already appeared.[15] Subsequent to it, other members of our laboratory have greatly extended the studies, both for *Cu*Co and for other systems, and have added to the theoretical analysis, but we will not discuss the extensions in this paper. Similar measurements at $T < T_K$ were made in *Cu*Ni ($T_K \sim 7000$ °K).[4] The *Cu*Ni results are reported elsewhere.[16] Our measurements were made by observing weak resonances, satellites to the main Cu resonance, arising from copper atoms which are near neighbors to Co or Ni in dilute alloys of these atoms.

A severe experimental complication which is encountered in most experiments on dilute magnetic alloys is the tendency of the magnetic atoms to form pairs and higher-order clusters during (and even after) sample preparation.[17,18] This is an unavoidable consequence of the metallurgical properties of these systems. The magnetic properties of such clusters are very different from those of the isolated magnetic atoms which the experiment is designed to study. Thus, measurements of bulk, averaged properties (e.g., resistivity, susceptibility, host NMR linewidth) can be strongly influenced by even a small number of such clusters and great care has to be taken to determine the true behavior of isolated impurities.[17,18]

Such difficulties can be avoided in satellite NMR studies for two reasons. First, since resonance is a spectroscopic method, lines of different species can exist together and be identified as being from different species through the concentration dependence of their intensities. Second, the statistics of pair or higher-order cluster formation cause these spectra to be smeared in frequency since there are so many ways of forming clusters of a given size. We have in fact found no such lines which we can attribute to such clusters.

The satellites were first discovered by one of us (D.C.L) using an apparatus that operated at fields below 10 kG. D.V.L. extended the results to 60 kG and to 450 °K using a different apparatus. We present the results of both on *Cu*Co in this paper, as well as a brief description of the high-field rig. The low-field rig has been described previously.[16] The samples were prepared by J.B.B. assisted later by Thomas Stakelon.

In Sec. II we discuss the experimental method. In Sec. III we present a discussion of the experimental results. The results are summarized in Sec. IV.

II. EXPERIMENTAL METHOD

A. Low-temperature apparatus

For runs below room temperature and above 15 kG the following apparatus was used. The magnet was a 63-kG Westinghouse superconducting solenoid specifically designed for NMR work. The magnet homogeneity was about an order of magnitude better than the narrowest resonance lines encountered in *Cu*Co. The rf section of the spectrometer was very similar to the steady-state single-coil hybrid-tee apparatus described previously,[16] with the following exceptions. For operation of the sample chamber at liquid-He temperature, the Dewar configuration made it necessary that the NMR sample probe be 4 ft long. The capacitance of such a long probe is a severe problem at higher frequencies. A very quiet and stable tuning arrangement was achieved as follows. A family of probe heads was made, each containing an appropriate coil and fixed capacitors, chosen so that for a given set of sample Q and frequency conditions, the probe head was nearly matched to 50 or 100 Ω. The probe cable was part of a tuned transmission line (GR rigid 50-Ω air line) where the fine tuning could be accomplished with trimmer capacitors at appropriate positions on the line. To increase stability it was necessary to pot the probe head assemblies with General Electric RTV silicon rubber compound.

Another difference between this apparatus and the low-field rig was the use of a low-noise wide-band (10–110 MHz) preamplifier rather than a tuned preamplifier. The wide-band feature offered a great deal of convenience in changing frequencies without any apparent sacrifice in signal-to-noise ratio. An appropriate low-pass filter was used after the preamplifier to cut out the higher harmonics of the rf drive. Such a wide-band scheme requires rather low rf gain (31 dB) to avoid instabilities and consequently a sensitive lock-in amplifier (PAR HR-8) was needed.

The modulation coil was wound directly on the probe. Modulation amplitudes of up to 30 G peak-to-peak could be obtained at 150 Hz.

B. High-temperature apparatus

For runs between 300 and 450 °K, the Dewar for the superconducting solenoid was converted so that the bore was open to room-temperature access at

both the top and bottom. This allowed a 1-ft long probe to be inserted from the bottom of the magnet so the tuning could be accomplished outside of the Dewar just as in Ref. 16. A modification from that reference was the use of low-inductance trimmer capacitors and GR high-frequency tuning elements. The sample was electrically heated and the temperature measured and regulated with a PAR automatic platinum-resistance thermometer.

C. Samples

The alloys were prepared by melting a 99.999%-pure copper metal with 99.99%-pure cobalt in appropriate concentration ratios in an argon atmosphere in an induction furnace (1200–1260 °C) for 1–2 h. The ingot was then quenched, swaged, and annealed at 1010 to 1060 °C for 3 to 4 days. The annealed ingot was quenched into ice water and ground into 400-mesh powder with a tungsten-carbide cutter. Some samples were annealed after filing (Ref. 16), but no variation in satellite position was noted, so this final anneal was skipped for most samples.

D. Experimental procedure

Nuclear-magnetic-resonance measurements were made between 6.4 and 9.2 MHz with the spectrometer described in Ref. 16 and at 32 and 70 MHz with the spectrometer described here. At 1.4, 4.2, and 77 °K the sample was in contact with the liquid helium or liquid nitrogen. For higher temperatures the sample chamber was evacuated and the sample temperature measured with a platinum resistance thermometer. Attainment of thermal equilibrium was determined by waiting for minimum drift of the very critical rf balance condition. The 150-Hz modulation was set equal to the Cu-main-line width for optimum signal-to-noise ratio with acceptable distortion. When a satellite was located, the modulation was reduced to determine the true linewidth.

For runs below 10 kG a home-built improved Pound box was used for magnetic-field-strength measurements. For runs with the superconducting solenoid the frequency separation between the satellite and main line was determined by noting the change in the spectrometer frequency necessary to move the main line to the position on the sweep previously occupied by the satellite with the magnet in persistent mode and the sweep unchanged. As pointed out in Ref. 16, careful adjustment of the rf phase is an important step in resolving satellites near the main line. Satellite positions are taken to be the distance between the zero crossings of the derivatives of the satellite and main line with the same phase settings. This is straightforward for large separations, but involves some uncertainty for satellites close to the main line.

III. EXPERIMENTAL RESULTS

A. Measurement of $\sigma(\vec{r})$

All nuclei in a metal experience a shift in their resonance frequencies due to the interaction with the conduction electrons. This is the well-known Knight shift.[19] If, however, the conduction-electron-spin density $\sigma(\vec{r})$ is not uniform throughout the metal, some nuclei will experience different Knight shifts than others. This gives rise to a spectrum of resonance lines corresponding to the various inequivalent positions in the material. In the case of a dilute alloy of Co dissolved in Cu, the Cu nuclei which are near neighbors to Co atoms have a different Knight shift than the Cu nuclei far from Co atoms. Since the Co concentration is small, typically less than 0.5 at.%, the resulting spectrum is a strong resonance (the main line) due to the Cu which are far from the Co and a very weak satellite resonances due to the Cu which are near neighbors of Co atoms. Inhomogeneities in both the conduction-electron spin density and charge density will contribute to a change in the Knight shift. We expect to find, however, that the spin-density effect dominates for magnetic impurities.

Quadrupole interactions with the electronic-charge-density inhomogeneities will produce similar satellite spectra. One can distinguish between quadrupole and magnetic spectra by the magnetic-field dependence of the satellite separations from the main line.[16] Such tests show that the satellite spectra in this paper are all due to spatial variation in the Knight shift.

A typical satellite resonance is shown in Fig. 1. This is a derivative of the absorption signal. In order to locate the zero crossing of the derivative,

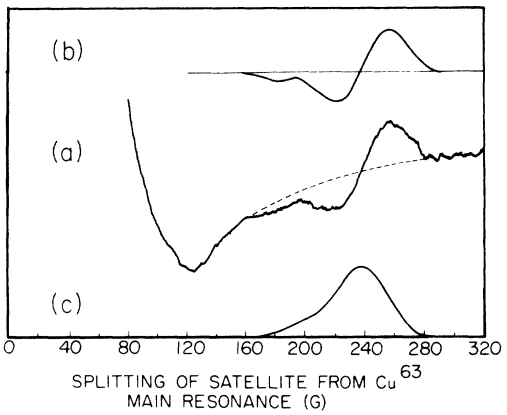

FIG. 1. Satellite resonance due to Cu^{63} nuclei which are first neighbors to a Co impurity. $H = 63$ kG, 0.1-at.% Co, 4.2 °K. (a) Output of signal averager; dashed line is estimated baseline. (b) Baseline subtracted from data. (c) Integral of (b).

the proper baseline must be determined. The criterion used to choose the baseline, as shown in Fig. 1, is to require that the integral of the derivative signal approach zero on both sides. Figure 2 is a summary of all the satellite data at 4.2 °K. No variation in position was observed as a function of Co concentration in samples of 0.05, 0.1, 0.3, 0.5, and 0.7-at.% Co. From the slope of the satellite positions versus magnetic field we determine the quantity $\Delta K/K$, which is the ratio of the difference between the Knight shifts of a satellite and bulk Cu divided by the shift of bulk Cu (which is the same as pure Cu). Two satellites are observed on the high-field side of the main line with $\Delta K/K = -1.65 \pm 0.02$ and $\Delta K/K = -0.31 \pm 0.01$ at 4.2 °K. Another satellite appears on the low-field side of the main line with $\Delta K/K = 0.82 \pm 0.01$ at 4.2 °K. All data reported is for Cu^{63}; identical spectra are observed for Cu^{65}.

In order to correlate these spectra with $\sigma(\vec{r})$, one must know which crystallographic locations give rise to the various satellites. Positive identification of the satellite due to the nearest neighbors of Co impurities can be obtained in three ways. The first is by the technique of spin-echo double resonance (SEDOR). One of us (J.B.B.) has used SEDOR to identify the satellite with $\Delta K/K = -1.65 \pm 0.02$ at 4.2 °K as being from the nearest neighbors.[15,20] An independent check on this identification can be obtained from the line shape of the satellite resonance shown in Fig. 1. We attribute the asymmetry of this line to the direct dipole-dipole interaction between the Cu nuclei in this shell and the Co-electron magnetic moment. In the applied field H the cobalt has an induced magnetic moment χH which produces a magnetic field at a neighbor a distance r away ranging from $-\chi H/r^3$ to $+2\chi H/r^3$, depending on the orientation of the radius vector with respect to H, where χ is the magnetic susceptibility of the Co. For $\chi = 4.0 \times 10^{-27}$ emu/atom, the Co susceptibility,[17] $H = 63$ kG, $r = 2.55$ Å (the nearest-neighbor distance in pure copper) $\chi H/r^3$ is 15 G. We have attempted to reproduce the exact derivative curve of Fig. 1 with a computer calculation which computes the appropriate powder pattern, including a Gaussian smearing arising from the nuclear moments of the other Cu atoms. We can not exactly fit the shape of Fig. 1 if the assumed baseline is correct. Nevertheless, the best fit gives $\chi H/r^3 = 20.7$ G, 35% too large. Only the nearest neighbor could have such a large dipolar coupling. We show in Appendix A that the pseudo-dipolar coupling is probably only about 0.5 G and thus negligible.

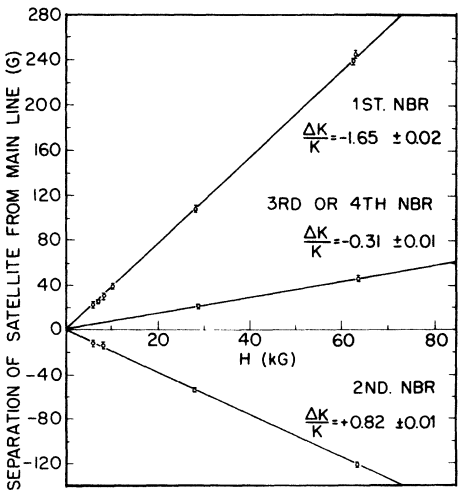

FIG. 2. Magnetic field dependence of satellite separations from main Cu^{63} line at 4.2 °K. The separations are concentration independent for $c < 0.7$ at.% Co.

Recently Stakelon in our laboratory has observed this satellite using single crystals of *Cu*Co and has verified the identification as arising from a first neighbor by studying the satellite position as a function of orientation of H with respect to the crystal axes.

The identification of the other two satellites at this point can only be made on the basis of the relative intensities. The satellite which we have called the second neighbor ($\Delta K/K = 0.82$) has about half the intensity of the first neighbor, while the satellite which we have called the third or fourth neighbor ($\Delta K/K = -0.31$) has an intensity which is equal to or greater than that of the first. Further SEDOR experiments at high magnetic fields should verify these identifications as should single-crystal studies which Stakelon is undertaking.

On the basis of these assignments, the data show that $\sigma(\vec{r})$ near the Co impurity atoms oscillates spatially with a period of about $2k_F r$ and decreases roughly as r^{-3}, (where k_F is the Fermi wave vector of Cu and r is the distance of the Cu atom giving rise to the satellite from the Co atom), as does the RKKY result[3] for $\langle \sigma_z(\vec{r}) \rangle$:

$$\langle \sigma_z(\vec{r}) \rangle = -\tfrac{9}{2}\pi (J_{sd}/E_F) F(2k_F r) \langle S_z \rangle \quad , \tag{1}$$

where

$$F(x) = (x\cos x - \sin x)/x^4 \quad , \tag{2}$$

and where the coupling of the conduction electrons to the spin $\vec{S}$ of the local moment is given by a Hamiltonian[3]

$$\mathcal{H} = -2J_{sd} \sum_j \vec{S} \cdot \vec{\sigma}_j \delta(\vec{r}_j) \quad . \tag{3}$$

Application of this formula to the observed $\Delta K/K$ values reveals two interesting facts. (i) The magnitude of the coupling can be explained by $J_{sd} = 1.5$ eV, a reasonable value as we describe below, but

(ii) the sign of the experimental coupling is opposite to the theoretical.

The general magnitude of J_{sd} has been estimated by Daybell and Steyert from the formula for the Kondo temperature[3]

$$k_B T_K = E_F e^{-1/(2|J_{sd}|\rho_1)} \quad , \tag{4}$$

where ρ_1 is the density of states of a given spin at the Fermi energy. Daybell and Steyert use $\rho_1 = 0.15$ $eV^{-1}\,atom^{-1}\,spin^{-1}$, but there is ambiguity about what value to use, since Eq. (4) applies to a half-full band with rectangular density of states. If we take a parabolic band, then

$$\rho_1 = (3/4E_F)(m^*/m) \tag{5}$$

vs $\rho_1 = (1/E_F)(m^*/m)$ for a rectangular band. Using $E_F = 7.0$ eV, $m^*/m = 1.38$,[21] and the parabolic band gives $\rho_1 = 0.15$ $eV^{-1}\,atom^{-1}\,spin^{-1}$. For $T_K \cong 1000$ K we get $|J_{sd}| = 0.76$ eV. For $T_K \cong 5000$ K we get $|J_{sd}| = 1.2$ eV. Either value is reasonable when compared to the 1.5 eV deduced from Eq. (1).

The fact that the sign of $\sigma(\vec{r})$ given by RKKY is opposite to the data, agrees with calculations by Geldart,[9] who shows that the RKKY expression is correct only asymptotically, i.e., beyond the tenth shell. The shape of $\sigma(\vec{r})$ in the local vicinity of the impurity is strongly influenced by the magnetic ion structure and the wave-number dependence of the scattering. A sample calculation in Ref. 9 shows a situation where the resulting $\sigma(\vec{r})$ has a sign opposite to that of RKKY for the first few neighbors, in qualitative agreement with our data.

From the measured $\Delta K/K$ values we can also determine the contribution to the total impurity susceptibility made by the three shells of neighbors giving rise to the satellites. Denoting the spin susceptibility per atom of the conduction electrons as χ_s, $\Delta K_i/K$ as the $\Delta K/K$ of the ith shell of neighbors, and Z_i the number of atoms in the shell, we have for the extra susceptibility of a single center from polarized electrons on the neighbors

$$\chi_{\text{neighbor}} = \chi_s \sum_i \frac{Z_i \Delta K_i}{K} \quad . \tag{6}$$

Taking $\chi_s = 1.55 \times 10^{-29}$ emu/atom from Pines,[22] we get $\chi_{\text{neighbor}} = -3.4 \times 10^{-28}$ emu/atom if the satellites are ascribed to the first, second, and third shells, or -2.5×10^{-28} emu/atom if they are ascribed to the first, second, and fourth shells. Thus, the net result is a contribution to the susceptibility that is aligned antiferromagnetically relative to the Co spin and accounts for -8% or -6% of the total impurity susceptibility for the two assignments, in agreement with the neutron-diffraction studies of *Cu*Fe by Stassis and Shull.[14] Our data support the perturbation-theory results which predict a relative contribution of $-J\rho_1$ from the integral of $\sigma(\vec{r})^2$; they also agree with the result of Bloomfield, Hecht, and Sievert,[11] which is valid for $T < T_k$ and predicts a nonlocal antiferromagnetic contribution one order of magnitude less than the localized component. However, they disagree with the picture of $\sigma(\vec{r})$ put forward by Heeger and coworkers,[7,12] in which theoretical arguments and analyses of experimental results in *Cu*Fe suggest that the conduction-electron contribution to the total impurity susceptibility is half the total and is aligned ferromagnetically. Since this theoretical calculation was based on the Kondo-Applebaum theory in which defects were subsequently found, the theoretical result is suspect. Narath[3] has discussed the current experimental situation.

It is interesting to compare the $\Delta K/K$ values for *Cu*Co to that measured at the first neighbor site in *Cu*Ni, the next system in the periodic table. As pointed out in Ref. 16, the first neighbor shifts for *Cu*Co and *Cu*Ni are almost exactly in the ratio of the respective values of χJ, where χ is the magnetic susceptibility and J is the s-d exchange constant deduced from estimates of the Kondo temperature. Such a scaling with χJ is exactly that predicted by the RKKY approximation. Most of the change in going from Ni to Co arises from the χ. Since, as we discuss below, T_K of Co is ambiguous, χ is formed from both orbital and spin contributions, and the RKKY approximation is not accurate for the near neighbors, it is fortuitous that we should observe such close agreement. We can certainly conclude, however, that the relative shifts are quite reasonable.

B. Temperature dependence of satellite shifts

We have studied the temperature dependence of the satellite Knight shifts between 1.5 and 450 °K. Figure 3 shows the inverse Knight shift of the first neighbor satellite versus temperature. The other two satellites have essentially the same dependence, but with much larger error bars. We could detect no change in the ratios of the three satellite shifts versus temperature; the accuracy of these ratio measurements is about 20%. Note that the Knight shift data of Fig. 3 indicates a much weaker temperature dependence than the bulk susceptibility; both obey Curie-Weiss laws, but the satellite shift had $\Theta = 4700 \pm 1000$ °K, while the susceptibility follows $\Theta = 950 \pm 100$ °K.[23,24]

Schotte and Schotte give theoretical expressions for the susceptibility χ, which has the same functional form as numerical solutions of Anderson's theory. At high temperatures they find

$$1/\chi \propto 1 + T/T_k \quad , \tag{7}$$

but at low temperatures

$$1/\chi \propto 1 + (T/1.20T_k)^2 \quad . \tag{8}$$

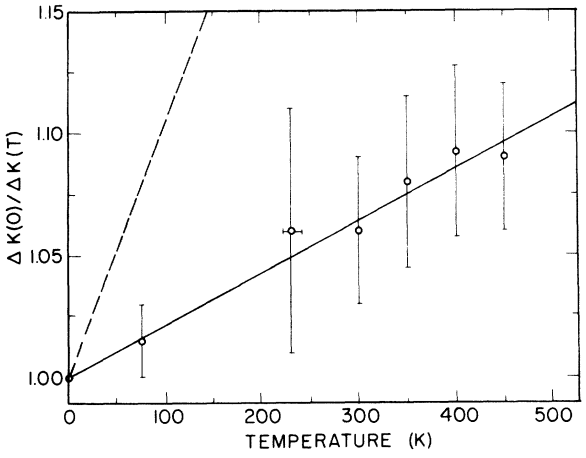

FIG. 3. Temperature dependence of first-neighbor-satellite inverse Knight shift. The other two satellites have the same temperature dependence but with much larger error bars. The line through data is Curie-Weiss law with $\Theta = 4700 \pm 1000$ °K. Dashed line: inverse bulk susceptibility normalized to 1.0 at $T = 0$ °K.

Applying Eq. (8) to the data at 450 °K, using the fact that $\Delta K \propto \chi$, gives $T_k = 1.6 \times 10^3$ °K. However, the data of $1/\Delta K$ vs T are better fit by straight line such as Eq. (7).

Gardner and Flynn[24] have studied the Knight shift of Cu atoms in molten alloys of *Cu*Co (at 1100 °C). The rapid diffusion causes the Cu atoms to measure the spatial average of the Knight shift $\overline{K}$. It varies linearly with Co concentration c. They find

$$\frac{1}{K}\frac{d\overline{K}}{dc} = -7.67 \quad . \tag{9}$$

From our data, we can compute $\overline{K}$ at helium temperature (4.2 °K) assuming that the only change in Knight shift from pure Cu occurs within the three shells we have observed. We get

$$\frac{1}{K}\frac{d\overline{K}}{dc} = -22.3 \text{ or } -18.6 \quad , \tag{10}$$

depending on whether we assign the satellite with $\Delta K/K = -0.31$ to the third or fourth shell. If Eq. (7) is assumed to hold from 4.2 °K to 1130 °C, this analysis gives Kondo temperatures of 960 or 750 °K, respectively.

C. Width of the main line

1. Temperature dependence

As pointed out earlier in this paper, the satellite-resonance technique makes it relatively straightforward to separate the effects due to single impurities from those due to impurity clusters. A satellite whose intensity goes linearly with concentration can be attributed to an isolated impurity, those varying with higher powers belong to pairs or larger clusters. On this basis we conclude all the satellites we have resolved are from isolated Co atoms.

On the other hand, measurements of susceptibility and resistivity[25] show interaction effects near the liquid-helium region. Tournier and Blandin[17] and Dreyfuss-Bourquard[17] interpreted the susceptibility in terms of one contribution from isolated Co impurities which was nearly independent of temperature and gave an extra susceptibility $\chi_1 = 4.0 \times 10^{-27} c$ emu/Cu atom. They also found a susceptibility due to pairs, $\chi_2 = 2.11 \times 10^{-24} c^2$ emu/Cu atom at liquid-helium temperatures, which had a Curie-Weiss temperature dependence with $T_K =$ 20 °K. A third contribution from triples or higher clusters had evidently a negligible T_K. For 0.5-at.% Co in Cu, $\chi_2 = 2.5\chi_1$ so pairs dominate the susceptibility. At temperatures far above 20 °K, however the singles dominate.

Figure 4 shows our data on the concentration and temperature dependence of the Cu main line. Note that the linewidth has a strikingly different temperature dependence from the satellite splitting. Yet we find the extra line breadth over pure Cu is proportional to H, and to c, hence arises from magnetic coupling to the impurities.

We have decomposed our measurements of the Cu main line assuming it has contributions from singles and pairs. For the singles, we take the temperature dependence of the satellite splittings (within experimental error of Curie-Weiss law with $T_K = 4700$ °K). For the pairs, we take $T_K = 20$ °K, so that the width ΔH (peak to peak of the derivative)

$$\Delta H = A/(T + 4700) + B/(T + 20) \quad . \tag{11}$$

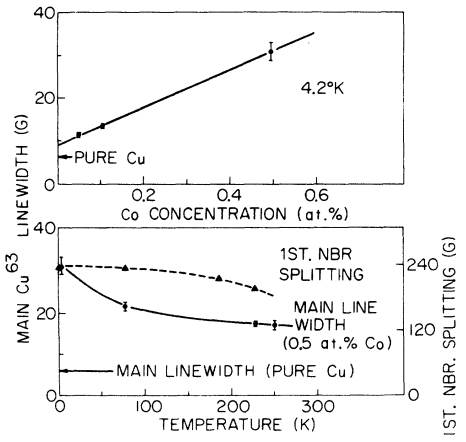

FIG. 4. Concentration dependence of the width of the main Cu^{63} resonance (peak to peak of the derivative) (top). Comparison of the temperature dependences of the width of the main Cu^{63} resonance and the satellite Knight shifts (bottom). $H = 63$ kG, $c = 0.5\%$.

We determine A and B by fitting the line width at 4.2 and 250 °K. In computing A and B, we have used the corrections of Sugawara,[26] who deconvoluted the pure copper contribution to experimental line width, and we have then used these corrections to recompute the experimental numbers. (Thus, a 7-G ΔH of pure copper contributes 1.4 G to the 31-G experimental width at 4.2 °K, and 2.4 G to the 17-G experimental width at 250 °K.) The results are given in Table I.

As can be seen, the decomposition into pair and single contributions nicely accounts for the temperature dependence of the line breadth. At 4.2 °K singles contribute 13.7 G and pairs 16.9 G, not quite the susceptibility ratio of 1/2.5. (Note that we have assumed that pairs give a Lorentzian line as do singles, making use of the facts that the convolution of two Lorentzians is itself Lorentzian, and that the experimental line breadth, when the natural copper contribution can be neglected, is Lorentzian.)

It is interesting to note that despite the success of the division of the line breadth into contributions from pairs and singles, the line breadth still is nearly linear in c. We need more data to get an accurate measure of the deviation.

Reasoning directly from our data, we conclude that pair effects are to be expected in the Cu line width for the system *Cu*Fe. At 1.3 °K, low magnetic fields, and $c = 250$ ppm, $\chi_2 = 2.5\chi_1$ for iron,[27] the same ratio we have for our 0.5-at.% Co in Cu sample. By analogy, we might expect about half the linewidth to arise from pairs and that it should drop rapidly above the T_K of the pairs, a number somewhere between 0 and 5 °K. We thus quantitatively support the proposal of Tholence and Tournier that the extra line broadening at low temperatures is attributable to pairs. Certainly the pair contribution must be included before one can draw conclusions about Kondo correlation effects.

Another aspect of significance is worth noting. In much of the literature, the concentration of single impurities c_1 is said to equal the concentration of cobalt atoms c. However, if there are Z neighbor sites which, if occupied, change the center from a single to a pair, we must assure that none of these sites is also occupied in order to say a cobalt is a single. Hence

$$c_1 = c(1-c)^Z \quad . \tag{12}$$

For c small, this becomes

$$c_1 = ce^{-Zc} \quad . \tag{13}$$

Tholence and Tournier state $Z = 520$ for pairs. Thus for $c = 1000$ ppm, $c_1 = 590$ ppm, a substantial correction. The difference represents pairs. This effect compensates the nearly c^2 pair contribution to give net result approximately linear in c.

2. *The magnitude of the linewidth*

Walstedt and Walker[28] have done computer analyses of the effect of the RKKY coupling on the linewidth and line shape at low concentrations. Assuming a Lorentzian line shape with half width at half-maximum Δ and an RKKY coupling for the field δH produced by one impurity at distance r,

$$\delta H(r) = (A_1/r^3)\cos(2k_F r + \phi) \quad , \tag{14}$$

where ϕ is a phase angle, they find

$$\Delta = (16\pi A_1/3a^3)c_1 \quad , \tag{15}$$

where a is the lattice constant of the face-centered-cubic lattice, the structure they have considered.

Applying these expressions to our linewidth data of Table I at 63 kG and 4.2 °K gives $A_1 = 6639$ G Å^3, which gives a first-neighbor splitting of 351 G (inserting a $\phi = \pi$ into the full RKKY expression to get the right sign of coupling) versus an observed value of 239 G. Since we do not expect the RKKY to hold accurately near to the impurity, this result shows only that the line-width data are reasonable in terms of the first-neighbor splittings. The linewidth give $J_{sd} = 2.2$ eV using Eqs. (1), (2), (14), and (15).

For pairs, we might expect

$$\delta H(\vec{r}) = \frac{A_2}{2}\left(\frac{\cos(2k_F r_1 + \phi)}{r_1^3} + \frac{\cos(2k_F r_2 + \phi)}{r_2^3}\right) , \tag{16}$$

where r_1 and r_2 are the respective distances of the atoms of the pair to the point $\vec{r}$. This equation defines A_2. When $r \gg L$, the distance between the atoms of the pair, we get

$$\delta H(\vec{r}) = (A_2/r^3)\cos(2k_F r + \phi)\cos(k_F L\cos\theta) \quad , \tag{17}$$

TABLE I. Theoretical and experimental contributions to the line breadth of the main Cu resonance (at 63 kG and 0.5%-Co concentration).

Temperature (K)	4.2	77	230	250
Pure Cu contribution (G)	1.4	1.7	2.3	2.4
Contribution from single Co (G)	13.7	13.5	13.1	13.1
Contribution from Co pairs (G)	16.9	4.2	1.6	1.5
Total theoretical line breadth (G)	32.0	19.5	17.1	17.0
Experimental line breadth (G)	31 ± 2	21.4 ± 1	17.2 ± 0.5	17 ± 1

where θ is the angle between the pair axis and $\vec{r}$.

For *Cu*Co the evidence is that a pair consists of first neighbors, so

$$\cos(k_F L\cos\theta) = \cos(3.46\cos\theta) \quad . \tag{18}$$

This term will mean that on a sphere of fixed r the effective A is reduced from A_2 to $A_2|\cos(3.46\cos\theta)|$ or, when averaged over θ, $0.67A_2$. In the s-d model, A is proportional to χJ, where χ is the susceptibility of a single unit (pair or single). In terms of the total susceptibility of all singles χ_1, and all pairs χ_2, we have

$$\Delta_1/\Delta_2 = \chi_1 J_1/0.67\chi_2 J_2 \quad . \tag{19}$$

$\chi_2/\chi_1 = 2.5$ at 4.2 °K. Using $T_K = 1000$ or 5000 °K for singles, and 20 °K for pairs in Eq. (4) gives $J_1/J_2 = 1.87$ or 2.9, respectively, or $\Delta_1/\Delta_2 = 1.1$ or 1.7 versus the experimental ratio 0.8. We conclude, therefore, that the magnitude of the pair contribution deduced from the temperature dependence of the line width is reasonable in terms of measured magnitudes and temperature dependence of the magnetic susceptibility. It is tempting to take this as evidence against the 5000 °K T_K.

IV. CONCLUSIONS

We have resolved three satellites to the main line of Cu in *Cu*Co alloys. The satellite shifts are proportional to magnetic field and are due to the indirect magnetic interaction with the Co atom. From spin-echo double resonance, line-shape, and single-crystal studies we can identify the satellite with the largest shift ($\Delta K/K = -1.65 \pm 0.02$ at 4.2 °K) as due to the Cu atoms in the first shell of neighbors near a Co atom. By relative intensities we identify the second neighbor ($\Delta K/K = 0.82 \pm 0.01$ at 4.2 °K) and the third or fourth neighbor ($\Delta K/K = -0.31 \pm 0.01$ at 4.2 °K). This shows that the electron spin density near the Co atoms oscillates with a period of about $2k_F r$ and falls off roughly as r^{-3}.

The magnetic shift for the first neighbor is an order of magnitude larger than for *Cu*Ni and almost exactly scales in the ratio χJ, as would be expected from simple theories such as RKKY. The sign of the coupling is opposite that of RKKY, in agreement with calculations of Geldart.

The contribution to the impurity susceptibility made by the three shells of neighbors observed in *Cu*Co is aligned antiferromagnetically relative to the Co spin and is 8% of the total impurity contribution to the susceptibility. This is consistent with neutron diffraction studies of *Cu*Fe, with perturbation theory, and with the theoretical results of Bloomfield *et al.*

The temperature dependence of the satellite shifts has been measured from 1.5 to 450 °K and is found to be much weaker than the bulk susceptibility. The best fit to the data is a Curie-Weiss law with $\theta = 4700 \pm 1000$ °K, though a quadratic dependence with $\theta = 1560$ °K is not ruled out.

The width of the main line is decomposed into two components by assigning each component a known temperature variation. One component Δ_1 due to isolated Co is assigned the temperature dependence of the satellite splittings. The other component Δ_2 is given the temperature dependence of the contribution of Co pairs χ_2 to the susceptibility. The decomposition at two temperatures accounts for the linewidth at all temperatures. The theory of Walstedt and Walker shows that Δ_1 roughly agrees with what one would predict from the satellite splittings, and that Δ_1/Δ_2 is reasonable in terms of the magnitude and temperature dependence of χ_1 and χ_2.

The results scaled to *Cu*Fe show that much of the observed low-temperature anomaly in width arises from pairs. This correction must be made before one can assert that there is evidence in that system for Kondo correlation effects.

We wish to thank Thomas Stakelon for assistance in sample preparation and permission to quote his single-crystal results.

APPENDIX A: ESTIMATE OF THE PSEUDODIPOLAR COUPLING OF THE Co TO THE NEIGHBORING Cu

A pseudodipolar coupling arises between the Co electrons and the nuclei of neighboring Cu because the conduction electrons possess p- or d-like character in the vicinity of the copper neighbor, largely as a result of the orthogonalization of the conduction electron wave functions to those of the core electrons. Using coordinates centered on a copper, consider the pseudodipolar term

$$\mathcal{H}_{\text{pseudodip}} = \gamma_e \gamma_n \hbar^2 \sum_j \sigma_{zj} \frac{3\cos^2\theta_j - 1}{r_j^3} I_z \tag{A1}$$

coupling the z component of the nuclear spin I_z with the z component of conduction electron spin σ_{zj}. r_j is the magnitude of the radius vector $\vec{r}_j$ from the copper nucleus to electron j, and θ_j is the angle between r_j and the z axis. We call this a pseudodipolar coupling because the polarization of the σ_{zj}'s arises from the J_{sd} coupling to the cobalt spin moment.

Averaging over the conduction electron wave functions gives an effective magnetic field

$$H_{eff} = -\gamma_e \hbar \langle \sigma_z [(3\cos^2\theta - 1)/r^3] \rangle \quad , \tag{A2}$$

where the angle brackets signify the wave function average. Assuming the spatial part to vary slowly with the electron energy in the region of energy for which there is spin polarization gives a pseudodipolar magnetic field

$$H_{\text{pseudodip}} = -\gamma_e \hbar \langle \sigma_z \rangle \langle (3\cos^2\theta - 1)/r^3 \rangle \quad . \tag{A3}$$

Using the fact that

$$-\gamma_e \hbar \langle \sigma_z \rangle = \chi_{\text{atom}} H \quad , \tag{A4}$$

where χ_{atom} is the contribution of the conduction electrons within the Wigner Seitz polyhedron containing the Cu atom to the total susceptibility of the impurity, and that

$$\chi_{\text{atom}}/\chi_s \cong \Delta K/K \quad , \tag{A5}$$

where χ_s is the conduction electron spin susceptibility per atom, we get

$$H_{\text{pseudodip}} = \chi_{\text{atom}} H \langle (3\cos^2\theta - 1)/r^3 \rangle \quad . \tag{A6}$$

The nonvanishing of the term $\langle (3\cos^2\theta - 1)/r^3 \rangle$ also gives rise to a quadrupolar coupling. The quadrupolar coupling frequency ν_Q *from this source* is

$$\nu_q = [3e^2Q/2I(2I-I)h] \langle (3\cos^2\theta - 1)/r^3 \rangle \quad , \tag{A7}$$

where we have omitted a Sternheimer factor, since the principal contribution should come from within the atom under observation.

For Cu we get

$$\nu_Q = 2.785 \times 10^{-18} \langle (3\cos^2\theta - 1)/r^3 \rangle \quad , \tag{A8}$$

so that

$$H_{\text{pseudodip}} = \chi_s (\Delta K/K) H \nu_Q / 2.785 \times 10^{-18} \quad . \tag{A9}$$

Of course, there are other contributions to ν_Q, but there is no evidence that ν_Q is significantly larger than 1 MHz, the measured value in *Cu*Ni.[16] Using this value, $\chi_s = 1.55 \times 10^{-29}$ emu/atom from Pines[22] and $H = 60$ kG gives $H_{\text{pseudodip}} = 0.5$ G, only a few percent of the direct contribution.

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