Measurement of Electron Spin Density near Co Atoms in Cu†

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We report NMR and double resonance studies of *Cu*Co in which we resolve 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 versus temperature from 1.5 to 450 K.

The properties of isolated $3d$ atoms dissolved in nonmagnetic host metals have been the subject of intense interest for several years.[1-8] This general class of problems has been referred to by many authors as the Kondo problem or Kondo effect. An important aspect of this problem is the spatial form of the conduction-electron spin density in the vicinity of the magnetic impurity atom. It is generally believed that above the Kondo temperature T_K this shape is approximated asymptotically by the well-known Ruderman-Kittel-Kasuya-Yosida (RKKY) perturbation-theory result.[2] However, close to the impurity, i.e., inside about the tenth shell, the shape is strongly influenced by the magnetic ion structure and the wave-number dependence of the scattering.[9] Below T_K several theoretical predictions have been made,[2,7] but there is no general agreement as to which, if any, might be the correct result.

We report here nuclear magnetic resonance and double resonance experiments which give detailed information about the electron spin polarization in the vicinity of Co atoms dissolved in a Cu host. We study directly or indirectly the resonance of the host Cu nuclei. In addition to the bulk Cu resonance, we observe three very small "satellite" resonances which we attribute to the Cu nuclei which are near neighbors to a Co impurity. By measuring the position of these satellite resonances relative to the large main resonance we obtain a measure of the electron spin density at these neighboring positions. All measurements are at temperatures well below T_K.

An advantage of studying resolved resonances is that it enables us to observe isolated Co atoms even in the presence of pairs and larger clusters.

Because of its rather high Kondo temperature ($T_K \sim 1000$ K),[4] the *Cu*Co system has not been as extensively studied as systems such as *Cu*Fe and *Au*V. However, as pointed out by Daybell and Steyert,[4] earlier studies of the susceptibility, resistivity, specific heat, and thermopower of *Cu*Co indicate a behavior qualitatively similar to *Cu*Fe ($T_K \sim 30$ K) but with a Kondo temperature of about 1000 K. Such a large variation in Kondo temperature is reasonable in view of the large difference in T_K between *Cu*Fe and *Cu*Mn ($T_K < 1$ K).[4,10] This, coupled with the fact that Co is immediately adjacent to Fe in the periodic table, suggests that a thorough study of *Cu*Co is of interest to the Kondo problem. A direct measurement of the conduction-electron spin density in *Cu*Fe, *Cu*Mn, and *Cu*Cr would be of great interest, also; unfortunately, such experiments appear to be very difficult to do.

We describe experiments by three of us. D.C.L. made the initial discovery of two satellites using magnetic fields H less than 10 kG. D.V.L. performed the experiments at higher magnetic fields. J.B.B. performed the spin-echo double resonance work and, assisted in the later stages by T. Stakelon, prepared the samples.

A typical satellite resonance is shown in Fig. 1.

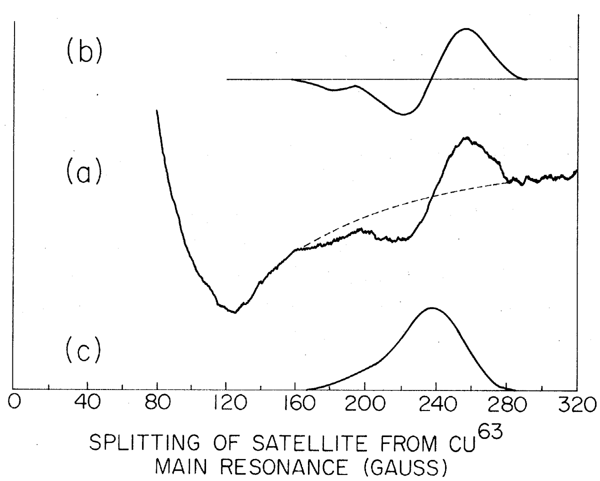

FIG. 1. Satellite resonance due to Cu^{63} nuclei which are first neighbors to a Co impurity. $H = 63$ kG, 0.1 at.% Co, 4.2 K. (a) Output of signal averager; dashed line is estimated baseline. (b) Baseline subtracted from data. (c) Integral of (b).

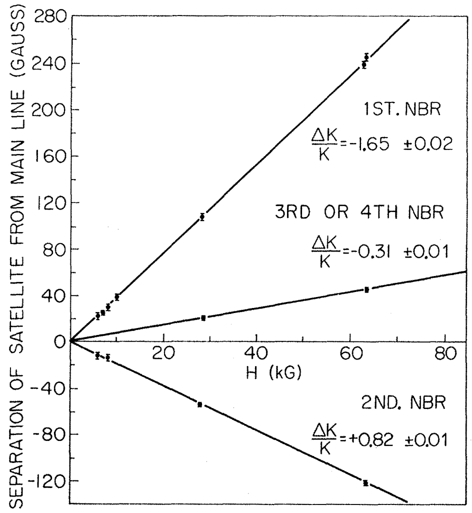

FIG. 2. Magnetic field dependence of satellite separations from main Cu^{63} line. 4.2 K. The separations are concentration independent for $c < 0.7$ at.% Co.

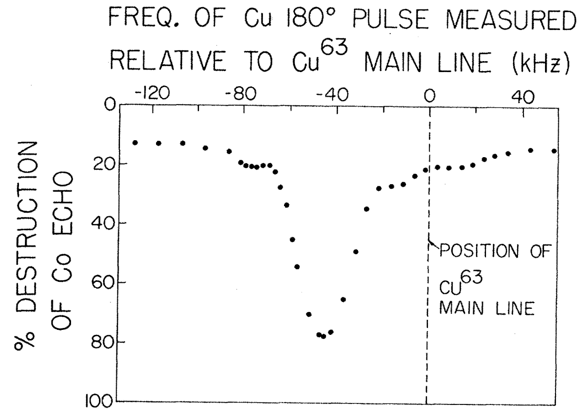

FIG. 3. Typical spin-echo double-resonance spectrum: Co echo amplitude versus frequency of Cu 180° pulse. 0.5 at.% Co, 10 kG, 1.5 K. Large destruction is due to the first shell of neighbors.

We have observed these satellites in powder samples of different Co concentrations (0.05, 0.1, 0.3, 0.5, and 0.7 at.% Co) and have found no variation in position. Figure 2 shows the magnetic field dependence of the satellite positions relative to the main Cu resonance which is unshifted relative to pure Cu metal. Such a linear dependence indicates that the three sets of Cu nuclei corresponding to these three satellites experience Knight shifts which are different from Cu nuclei which are far from a Co impurity.

The magnetic field dependence in Fig. 2 also shows that electric quadrupole effects are small enough in *Cu*Co to give a negligible contribution to the position of the satellite resonances. This is a rather surprising result. Our work in *Cu*Ni [11] as well as work in *Al*Mn [12] indicates that electric quadrupole effects can be quite sizable in these types of systems.

The identification of the satellites is a most important aspect of this work. Positive identification of the satellite corresponding to the first shell of Cu nuclei nearest to a Co impurity has been obtained from two pieces of evidence. The first makes use of the technique of spin-echo double resonance.[13] Figure 3 shows a typical spectrum of Co echo amplitude versus Cu 180° pulse frequency. Note that the large echo destruction occurs at a position corresponding to one of the satellites in Fig. 2 and that little destruction is evident at the Cu bulk resonance frequency. Analysis of the amount of destruction versus time between echo pulses shows that the destruction is caused by Cu nuclei which are nearest neighbors to Co impurities. The second piece of evidence is the line shape of the satellite resonance shown in Fig. 1. The asymmetry of this line is due to the direct dipole-dipole interaction between the Cu nuclei in this shell and the Co electron magnetic moment. The splitting is 30% larger than that calculated at the first neighbor from the measured value for the single Co susceptibility.[14] Only the nearest neighbor could have such a large asymmetry.

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 has about half the intensity of the first neighbor, while the satellite which we have called the third or fourth neighbor has an intensity which is equal to or greater than that of the first. Further work with spin-echo double resonance at high magnetic fields should verify these identifications.

On the basis of these assignments, the satellite Knight shifts presented in Fig. 2 show that the electron spin density near the Co impurity atom 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 from the Co atom. From the data in Fig. 2 we can also show that the conduction electrons on these three shells of neighbors contribute about 8% of the total impurity susceptibility due to isolated Co atoms[14] and that this contribution is aligned antiferromagnetically relative to the Co spin. This is in agreement with neutron diffraction studies of *Cu*Fe,[15] but disagrees with the in-

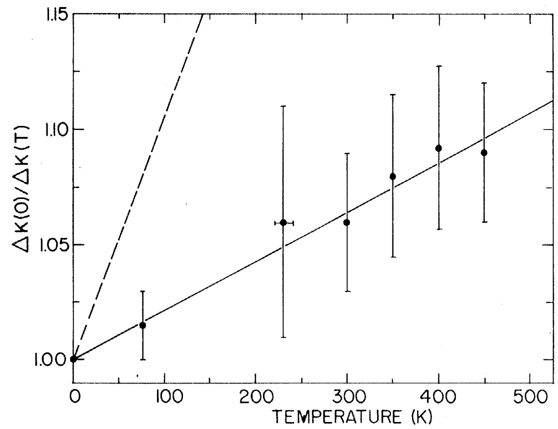

FIG. 4. Temperature dependence of first-neighbor–satellite inverse Knight shift. Line through data is Curie-Weiss law with $\theta = 4700 \pm 1000$ K. Dashed line is inverse bulk susceptibility normalized to 1.0 at $T = 0$ K.

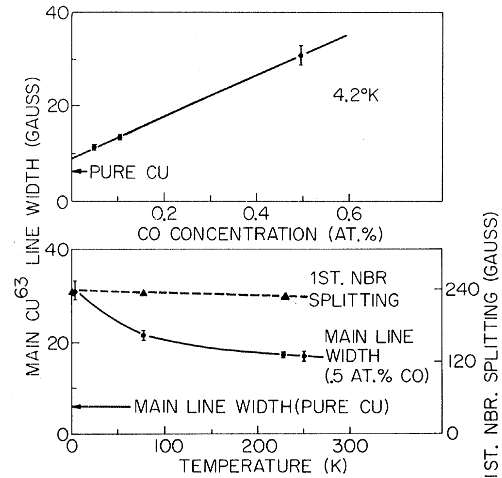

FIG. 5. Concentration dependence of the width of the main Cu^{63} resonance (top). Comparison of the temperature dependences of the width of the main Cu^{63} resonance and the satellite Knight shifts (bottom). $H = 63$ kG.

terpretation of other experimental results on *Cu*Fe and with calculations based on the Appelbaum-Kondo ground state, both of which indicate that the conduction-electron contribution to the total impurity susceptibility is half of the total and is aligned ferromagnetically.[7]

We have studied the temperature dependence of the satellite Knight shifts between 1.5 and 450 K. Figure 4 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. Note that the first-neighbor Knight shift has a much weaker temperature dependence than the bulk susceptibility: Both obey Curie-Weiss laws but the satellite shift has $\theta = 4700 \pm 1000$ K while the susceptibility follows $\theta = 950 \pm 100$ K.[16,17] A quadratic temperature dependence, i.e., $\Delta K^{-1} \propto 1 + AT^2$, is not ruled out by our data, but a Curie-Weiss law is a better fit.

In Fig. 5 we present a comparison of the temperature dependences of the width of the main Cu resonance and the first-neighbor–satellite Knight shift. Note that the behavior is quite different, with the main linewidth exhibiting a much stronger temperature dependence in this region. Note also that the main linewidth appears to be linear in Co concentration. Thus it is apparent that even though there is a linear behavior of the linewidth, one should be cautious in concluding that the properties of the main line are representative of single impurities.[7,18]

Professor Slichter expresses his appreciation to Dr. Lang for leading the group during the academic year 1970–1971 when Slichter was on sabbatical leave, and for at all times playing a crucial role as advisor to the others.

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Systematics of Conduction in a Band Tail*

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Systematic trends in the transport properties of a series of slightly Eu-rich EuS crystals, which strongly suggest that conduction occurs in a band tail, are reported and analyzed. A quantitative model for transport in band tails is developed. The model achieves good agreement with the high-temperature resistivity and Hall coefficient of our samples, and gives accurate predictions of their low-temperature properties.

In this Letter we report transport measurements, on nonstoichiometric EuS, which afford considerable insight into the general phenomenon of nonmetallic electronic conduction in disordered materials.[1] A series of n-type EuS single crystal samples was prepared in which carrier concentrations were varied from $<10^{18}$ to 10^{20} cm^{-3} by slightly increasing the Eu/S ratio. In several samples thermally activated conduction is observed at both high and low temperatures but the activation energy decreases markedly as $T \to 0$, suggesting that some form of variable-range hopping conduction (Ref. 1, p. 41) dominates at low temperatures.

All samples exhibit large, magnetic-field-dependent resistivity peaks at their ferromagnetic ordering temperatures. These peaks are quenched by a magnetic field, are similar to previously studied peaks,[2,3] and will not be discussed here.

Samples studied cover the transition between metallic and nonmetallic conduction in this system. Figure 1 presents the high-temperature data, resistivity and Hall coefficient, for all samples. These data may be described approximately by the expressions $\rho = \rho_\infty \exp(\Delta_\rho/kT)$ and $R = R_\infty \times \exp(\Delta_H/kT)$. Table I lists experimental parameters obtained in this way. Systematic trends are evident both in activation energies and in the prefactors. The resistivity activation energy, Δ_ρ, decreases from 28.5 mV for sample a to 0 for sample f, while $N_H \equiv 1/Re$ increases over two factors of 10. Both the Hall activation energy Δ_H and the ratio Δ_H/Δ_ρ decrease as well.

It proves impossible to reconcile the high-temperature resistivities and Hall data with a description of conduction by activation from donor states to the bottom of a well-defined conduction band or of conduction in a narrow donor band. We shall show, instead, that these data are consistent with a model in which random potential fluctuations smear the conduction band edge into a

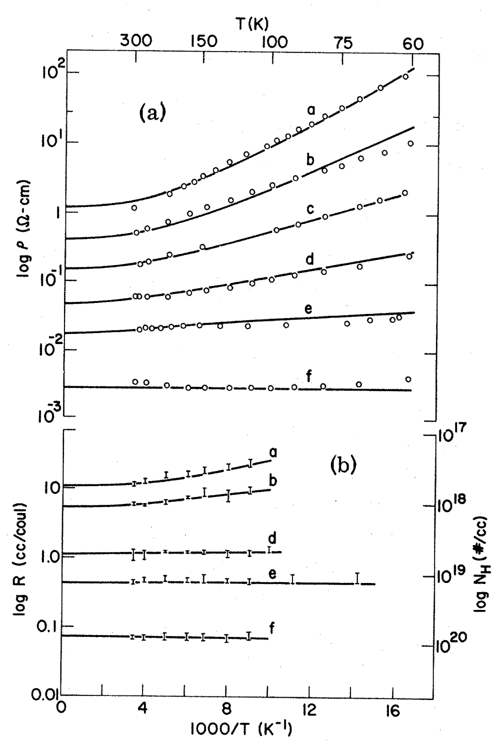

FIG. 1. (a) Logρ versus $1/T$, (b) log$R$ (Hall constant) and log$N_H \equiv \log(1/Re)$ versus $1/T$.