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NMR STUDY OF THE ELECTRON SPIN DENSITY NEAR IRON GROUP ATOMS IN Cu*

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ABSTRACT

We have observed the nuclear resonances of Cu atoms which are near neighbors to 6 of the 3d transition element impurities in dilute Cu alloys, systems of interest in the Kondo problem. The resonances appear as satellites split from the strong resonance of the distant Cu atoms. Their splittings yield the magnitude and spatial shape of the conduction electron spin magnetization. We have seen one shell of neighbors to Ni, two to V, three to Co, four to Cr and Mn, and five to Fe. The satellite in CuNi was studied at liquid helium temperatures in fields from 6 to 60 kG and those in CuCo from 1.5 to 450 K and 6 to 63 kG. To date we have studied CuV from 8 to 63 kG at liquid helium temperatures, CuCr and CuMn from 7 to 15 kG at 300 K, and CuFe from 7 to 61 kG and 77K to 330 K. The satellite positions are independent of concentration from about 500 ppm to 5000 ppm. The usual theoretical expressions for spin density are evaluated far from the impurity, where they depend only on the electrons at the Fermi surface. In contrast, to treat the near neighbors we have developed a d-wave phase shift analysis, in which conduction electrons of all energies are included to fit the experimental splittings in both the magnetic and non-magnetic cases.

INTRODUCTION

The detailed understanding of how an isolated magnetic atom behaves when dissolved in a non-magnetic metal, of the circumstances under which it possesses a permanent moment, has long been an area of interest. An important subclass of problems is concerned with the Kondo effect which may be characterized as the apparent change from the temperature independence susceptibility at low temperatures characteristic of an atom lacking a permanent moment to a near Curie's law behavior at high temperature characteristic of an atom possessing a permanent moment. Stimulated by the general interest in these dilute systems and in the Kondo effect, our colleagues and we have been studying dilute alloys of iron group atoms in copper.[1,2] In this paper we report on measurements of the spin polarization density, $\sigma(r)$, of the conduction electrons in the near vicinity of the impurity atoms. We report new results for V, Cr, Mn, and Fe. Previous results from our group have been reported on Co[2] and

If the repulsion is weak, no spontaneous splitting occurs, but when a magnetic field splits the up and down spin states, the repulsion enhances the splitting, leading to an enhanced spin magnetic susceptibility.

(1) Magnetic atoms. A straightforward analysis shows that at position R (measured from the impurity) the changes in Knight shift $\Delta K(R)$ relative to the Knight shift of pure Cu is given by

$$\frac{\Delta K(R)}{K} = \frac{\chi}{\chi_s^e} \sum_\sigma m_\sigma \int_0^{k_F} \rho_1(W_k)\, dW_k \frac{\left\{[n_2^2(kR) - j_2^2(kR)]\sin^2\delta_\sigma(k) - 2n_2(kR)j_2(kR) \sin\delta_\sigma(k)\cos\delta_\sigma(k)\right\}}{(\delta_+ - \delta_-)/2\pi} \quad (1)$$

where χ is the spin susceptibility of the impurity, χ_s^e is the spin susceptibility of the conduction electrons per unit volume, $\rho_1(W_k)$ the density of states of one spin orientation per unit volume. $\delta_\sigma(k)$ is the scattering phase shift for spin orientation σ for state "a". This result is similar to one utilized by Gardner and Flynn.[5] There is another term which we have omitted as unimportant for a strongly magnetic atom.

(2) Non-magnetic atoms. When there is no splitting of the up and down spin d-wave resonances, one can show

$$\frac{\Delta K(R)}{K} = 5\left\{[n_2^2(k_F R) - j_2^2(k_F R)]\sin^2\delta(k_F) - 2n_2(k_F R)j_2(k_F R)\sin\delta(k_F)\cos\delta(k_F)\right\} \quad (2)$$

$$- 5\,\frac{\rho_d U}{1-\rho_d U}\int_0^{k_F} \frac{\rho_1(W_k)}{\rho_1(E_F)} \left\{[n_2^2(kR) - j_2^2(kR)]\,\frac{\partial}{\partial E_\sigma}\sin^2\delta(k) - 2n_2(kR)\, j_2(kR)\,\frac{\partial}{\partial E}\sin\delta(k)\cos\delta(k)\right\}$$

Ni.[1] The measurements which we report in this paper were done at room temperature and liquid nitrogen temperature. Similar experiments to ours have been done by John Gardner on the system copper manganese. We appreciate his sending us reports prior to publication.

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[3] shift. If, however, the conduction electron spin density 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. For example 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%, the resulting spectrum is a strong resonance (the main line) due to the Cu which are far from the Co and 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 and find, however, that the spin density effect dominates for magnetic impurities.

EXPERIMENTAL METHOD

Some of the nuclear resonance apparatus used has been described in other papers.[1,2] In addition, for some of the data reported, we utilized a cross-coil Varian spectrometer through the courtesy of Professor T. J. Rowland. All of the data involved modulating the static field, lock-in detection, and averaging with a computer of average transients.

The sample preparation techniques are also described elsewhere.[1,2]

THEORY

In order to describe the spin polarization, σ (r), we utilize the Anderson[4] model. We distinguish two cases: (1) magnetic atoms, and (2) non-magnetic atoms. In the Anderson model, the d-states of the free iron group atom are mixed with the conduction band states becoming broadened when the atom is dissolved in Cu. As a result of the Coulomb interaction, the orbital states with up spin repel those with down spin. If the repulsion is strong, the up and down states split spontaneously, leading to a permanent magnetic moment even without an applied magnetic field. In the simplest Anderson theory, either the spin up state lies above the spin down state in energy or the reverse is true. We call these two ion configurations "a" and "b", respectively. "a" and "b" are still degenerate, but they are split by a magnetic field. If the field lies in the up direction, state "a" is lower in energy than "b".

one being at 57 ± 6G, the other at 129 ± 9G.

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where ρ_d is the density of d-states per impurity atom at the Fermi surface arising from the impurity, U is the Coulomb repulsion term of the Anderson theory, and E_σ the energy of the resonant level. $1/(1-\rho_d U)$ is the well-known enhancement factor of susceptibility.

As can be seen $\Delta K(R)/K$ depends on the location and width of the respective up and down spin states for both the magnetic and non-magnetic cases. Thus, in principle, sufficiently precise measurements of $\Delta K/K$ at enough non-equivalent neighbor sites would determine the width and location of the d-wave resonances.

EXPERIMENTAL RESULTS

The experimental results on $\Delta K/K$ to date are summarized in the Table. With the exception of our work on CuNi and CuCo we do not have experimental determinations of which neighbor shell goes with which $\Delta K/K$. We have studied CuV from 8 to 63 kG at liquid helium temperatures, CuCr and CuMn from 7 to 15 kG at 300 K, and CuFe from 7 to 61 kG and 77 K to 330 K. The satellite positions are independent of concentration from about 500 ppm to 5000 ppm.

Table I Experimental Values of $\Delta K/K$

Impurity	Temperature	Observed $\Delta K/K$
Fe	300 K	$-5.39 \pm .3$
		$-1.20 \pm .03$
		$-.36 \pm .02$
		$.28 \pm .03$
		$1.85 \pm .03$
Mn(a)	300 K	$-1.98 \pm .06$
		$-.53 \pm .08$
		$.34 \pm .03$
		$.58 \pm .09$
		$1.45 \pm .08$
Cr(b)	300 K	$-1.37 \pm .07$
	300 K	$.74 \pm .1$
	77 K	$1.52 \pm .09$
V	4.2 K	$-.66 \pm .03$

(a) An additional satellite was observed at 149 ± 9G on the low field side of the Cu main line resonance at 8.7 kG and moves to 167 ± 8G at 14 kG.

(b) Two additional satellites were seen on the low field side in CuCr. They are essentially field independent from 9 to 14 kG