SPIN POLARIZATION NEAR IRON GROUP ATOMS IN COPPER

JAMES B. BOYCE, THOMAS ATON, THOMAS STAKELON and CHARLES P. SLICHTER

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Ill. 61801, USA

ABSTRACT

Dilute solutions of iron group atoms in Cu are of interest in the general problem of the occurrence of magnetism and also for the Kondo effect. One way in which the Kondo effect manifests itself is through a magnetic susceptibility obeying a Curie–Weiss law $\chi = C/(T + T_K)$ (where C is a constant, T the temperature and T_K the so-called Kondo temperature), rather than Curie's law. Some theories and experiments have suggested that the spin polarization near the magnetic atom undergoes a significant change in shape when T is cooled below T_K.

We report n.m.r. measurement by Boyce and Aton of the conduction electron spin polarization $\sigma(\mathbf{r})$ at various copper sites near to V, Cr, Mn and Fe impurities in dilute (~ 0.1 %) alloys, extending the work of our colleagues Lang, Lo and Boyce on CuCo and CuNi. We also report results by Stakelon on single crystals of CuCo.

The Cu atoms near the magnetic atom experience a Knight shift (relative to the resonance of pure metallic Cu) which is proportional to $\sigma(\mathbf{r})$. We observe their weak resonance directly.

We give theoretical expressions relating $\sigma(\mathbf{r})$ to the magnetic properties of the impurity atom.

We present the recent results of Boyce, who has succeeded in following $\sigma(\mathbf{r})$ down through the 29 K Kondo temperature of CuFe in four neighbouring shells of Cu and has thus been enabled to test for the first time whether or not there is a shape change in $\sigma(\mathbf{r})$ associated with the Kondo condensation. He finds no shape change.

I. INTRODUCTION

Dilute solutions of iron group atoms in Cu are of interest in the general problem of the occurrence of magnetism and also for the Kondo effect. One way in which the Kondo effect manifests[1] itself is through a magnetic susceptibility obeying a Curie–Weiss law, $\chi = C/(T + T_K)$ (where C is a constant, T the temperature and T_K the so-called Kondo temperature), rather than Curie's law. Another way in which it manifests itself is through a minimum in the electrical resistance as one goes down in temperature. A minimum occurs near T_K. The presence of the magnetic atom polarizes the conduction electron spins in its vicinity. Some theories and experiments have suggested that the conduction electron spin polarization, $\sigma_z(r)$, near the magnetic atom undergoes a significant change in shape when T is cooled below T_K. This viewpoint arose because it had been proved that the ground state of a magnetic atom in a non-magnetic metal, at least for a spin 1/2 atom, should be a spin singlet in which the magnetic atom spin is paired off with the conduction electron spin.

The fact that magnetic atoms would broaden the resonance of the host nuclei far from the magnetic centre was first observed by Sugawara[2], who looked at the nuclear resonance of copper containing small amounts of iron-group atoms. He observed that the line broadened as the temperature was lowered, roughly following the magnetic susceptibility. If the breadth of the resonance, ΔH, is proportional to the magnetic susceptibility and if the magnetic susceptibility obeys the Curie–Weiss law, then a plot of the inverse of the linewidth versus the temperature should be a straight line whose intercept determines T_K. Alternatively one can plot the linewidth versus $1/(T + T_K)$ if T_K is known. Heeger and his colleagues studied[1] the nuclear resonance of copper containing small amounts of iron for which $T_K = 29$ K. Taking T_K from susceptibility measurements, he observed that the data at high temperature fit a straight line for this second kind of plot, but that at low temperature the line was substantially broader than given by this expression. He attributed this extra broadening to a 'Kondo condensation', some modification of the wave function associated with formation of the ground state singlet.

Various theoretical attacks on the problem gave differing results. The essence of the controversy, both theoretical and experimental, is whether the proper expression for the conduction electron spin density, $\sigma_z(r, T)$, in an applied magnetic field H is given by equation (1) or equation (2):

$$\frac{\sigma_z(r, T)}{H} = \chi_s(T) f(r) \tag{1}$$

$$\frac{\sigma_z(r, T)}{H} = \chi_s(T)\, g(r, T) \tag{2}$$

where $\chi_s(T)$ is the temperature-dependent spin susceptibility of the iron atom. Equation (1) says that the spin polarization resulting from the presence of a magnetic atom has the same temperature dependence as the spin contribution to the magnetic susceptibility of the impurity atom, and has a spatial dependence given by the temperature-independent function $f(r)$. Equation (2) implies that as the temperature is changed not only does the temperature variation of the spin susceptibility influence σ_z, but also the shape function, $g(r, T)$, changes, presumably as the temperature passes across the region of the Kondo temperature.

Several years ago our group decided to attempt to study $\sigma_z(r, T)$ by looking for the resonance of specific shells of neighbours which are very close to one or another of the magnetic impurities, e.g. the atoms in the first shell of neighbours, atoms in the second shell of neighbours, etc. These shells should give resonances which we call satellites because they are displaced from the strong resonance of the host nuclei far from the magnetic atom, the so-called main line. The satellites from neighbours to non-magnetic atoms in aluminium had been observed in our laboratory some years ago by Fernelius. Drain[3] had independently carried out extensive studies of such resonances. They are difficult to see because the metal samples are powdered and there is a quadrupole smear. Alloul *et al.*[4] had observed the magnetic effects of neighbours to Mn in Al.

Encouraged by these results, we resolved to attempt to find such satellites in the copper-based alloys. The reason for going to copper is that copper is a host for which the Kondo effect is known to occur, and for which one expects to have a good nuclear resonance from the host lattice. However, no one had reported seeing such satellites to magnetic atoms in copper. The strategy upon which we settled, carried out largely by James Boyce, was to make alloys of all the iron-group atoms in copper, with a range of concentration for each alloy which we judged optimum (from about 0.05 % to 0.5 % atom ratio). We did not know which if any alloy might give rise to satellites, and we did not know what concentration might give the best balance between having enough magnetic atoms to give us enough neighbours to see without causing too broad a resonance which would result at too high a concentration. The sample preparation job was a monumental task. We hoped to find a satellite in at least one alloy. Today we can report success for all the iron group V to Ni, inclusive.

The first resonances were found by Lo by steady state methods and by Boyce using nuclear double resonance. Their work together with that of David Lang has been published earlier (on the systems $\underline{Cu}Ni$ and $\underline{Cu}Co$)[5, 6]. We report here the new results on V, Cr, Mn and Fe. Some of the later samples were made by Thomas Stakelon. He made all of the single-crystal samples.

II. APPARATUS

The apparatus has been described in papers which have either appeared in *Physical Review* or are about to appear. They are all bridge-type apparatuses operating with 50 or 100 Ω lines with a hybrid tee as the bridge element. This enabled the apparatus to be tuned over a broad range of frequencies, as is necessary in this type of work. We have worked at fields from 6 kG to 63 kG and at temperatures from 1.2 K to 450 K.

The bridge is run as perfectly balanced as possible. Absorption versus dispersion or any desired linear combination is obtained by adjusting a phase shifter in a separate arm which injects oscillator voltage into the mixing stage of the r.f. amplifer. This feature is important, since one of the major difficulties in detecting resonances is that they occur on the tails of the main absorption line, which is often quite broad in these magnetic samples. It is very difficult to detect a weak resonance on the sloping background. A proper mixture of absorption and dispersion enables one to flatten the base line and thus see resonances which would otherwise be very difficult to see.

A second essential feature for detecting many of these lines is the ability to average for several days at a time. The use of a signal averager makes this possible. Signal averaging is a useful technique when one knows where to look. Thus, it is often possible to follow a resonance which is found under favourable circumstances—for example, when it is narrow at high temperatures—to less favourable circumstances where it is difficult to see as a result of being broad and weak. There is a substantial amount of advantage gained in seeing the weaker resonances by learning how to see the stronger ones.

III. THEORY

At temperatures well above the Kondo temperature we expect these systems to be described, at least in the first approximation, by Anderson's[7] theory of magnetic atoms. We have utilized this approach to calculate the spin polarization at position r away from an impurity atom. If we are dealing with a magnetic atom, application of the Anderson theory gives us an expression which is essentially that given previously by Gardner and Flynn[8]. (They do not quite give our expression, because they omit it from the stages of their calculation which involve an average over many neighbour positions, as is applicable to the case they studied of nuclear resonance in liquid metals.) We consider a host Knight shift K, and a change in Knight shift, $\Delta K(r)$, resulting from the spin polarization. The result is given in equation (3):

$$\frac{\Delta K(r)}{K} = \frac{\chi}{\chi_s^e}\sum_\sigma m_\sigma \int_0^{E_F} \rho_1(W_k)\,\mathrm{d}W_k \times \frac{\{[n_2^2(kr) - j_2^2(kr)]\sin^2\delta_\sigma(k) - 2n_2(kr)j_2(kr)\sin\delta_\sigma(k)\cos\delta_\sigma(k)\}}{(\delta_+ - \delta_-)/2\pi} \tag{3}$$

where χ is the spin susceptibility of the impurity, χ_s^e is the spin susceptibility of the conduction electrons per unit volume and $\rho_1(W_k)$ is the density of states of one spin orientation per unit volume, $\delta_\sigma(k)$ is the scattering phase shift for spin orientation σ for a state in which the total magnetic moment of the atom is parallel to that of the applied field. j_2 and n_2 are the two spherical Bessel functions of $l = 2$.

In the case of a nonmagnetic atom, i.e. one which does not possess a permanent moment, application of the Anderson theory leads to the expression given in equation (4):

$$\begin{aligned}\frac{\Delta K(r)}{K} &= 5\{[n_2^2(k_Fr) - j_2^2(k_Fr)]\sin^2\delta(k_F) - 2n_2(k_Fr)j_2(k_Fr)\sin\delta(k_F)\cos\delta(k_F)\} \\ &\quad - 5\frac{\rho_d U}{1-\rho_d U}\int_0^{E_F}\frac{\rho_1(W_k)}{\rho_1(E_F)}\mathrm{d}W_k\{[n_2^2(kr) - j_2^2(kr)]\frac{\partial}{\partial E_\sigma}\sin^2\delta(k) \\ &\quad - 2n_2(kr)j_2(kr)\frac{\partial}{\partial E_\sigma}\sin\delta(k)\cos\delta(k)\}\end{aligned} \tag{IV}$$

where U is the coulomb repulsion term between the up and down spin electrons on the magnetic atom and E_σ is the energy of the centre of the scattering resonance for electrons of spin σ. Time does not permit a discussion of these expressions. They should be viewed, however, as statements that the measurement of the Knight shift, $\Delta K/K$, gives one information about the scattering phase shift and its dependence upon energy as a result of the presence of the magnetic atom.

IV. RESULTS

Aton and Boyce have observed satellites in a number of systems. Their results are shown in *Table 1*[9]

Table 1. Experimental values of $\Delta K/K$

Impurity	Temperature	Observed $\Delta K/K$	Impurity	Temperature	Observed $\Delta K/K$
Fe	300 K	-5.74 ± 0.2	Mn†	300 K	-1.98 ± 0.06
		-1.20 ± 0.03			-0.53 ± 0.08
		-0.36 ± 0.02			0.34 ± 0.03
		0.28 ± 0.03			0.58 ± 0.09
		1.85 ± 0.03			1.45 ± 0.08
Cr‡	300 K	-1.37 ± 0.07	V	4.2 K	-0.66 ± 0.03
	300 K	0.74 ± 0.1			
	77 K	1.52 ± 0.09			

† 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.

‡ Two additional satellites were seen on the low field side in CuCr. They are essentially field independent from 9 to 14 kG, one being at 57 ± 6G, the other at 129 ± 9G.

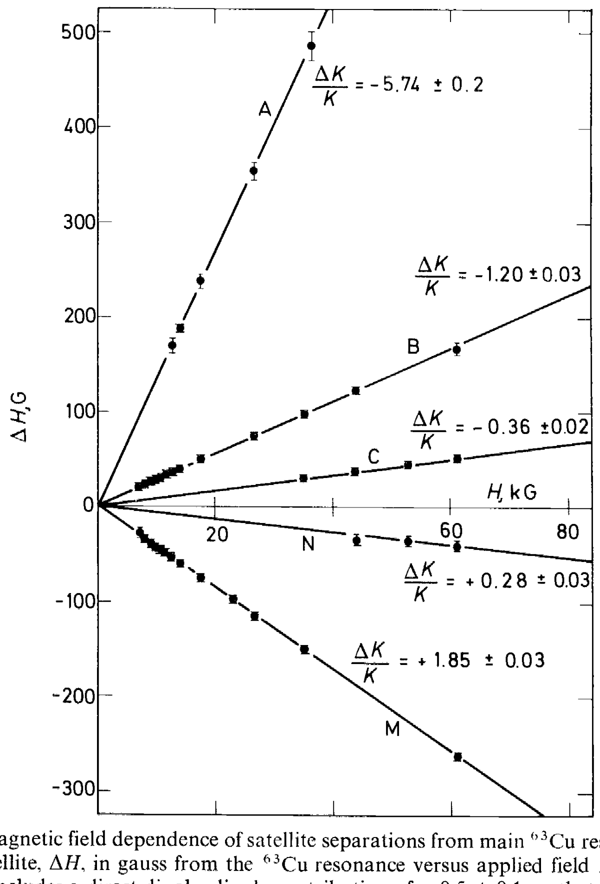

Figure 1. Magnetic field dependence of satellite separations from main ^{63}Cu resonance at 300 K. Shift of satellite, ΔH, in gauss from the ^{63}Cu resonance versus applied field H. The $\Delta K/K$ for satellite A includes a direct dipole–dipole contribution of -0.5 ± 0.1, so that the isotropic part of $\Delta K/K\,|_A = -5.24 \pm 0.3$

Most interesting from the point of view of the Kondo effect are the data obtained by Boyce and Slichter[10] on CuFe for which we can follow $\sigma_z(r, T)$ from above to below the Kondo temperature. These are shown in *Figures 1, 2* and *3*. *Figure 1* shows the splittings seen versus magnetic field at 300 K. We note that there are five satellites seen. It is our belief that satellite A arises from the first neighbour and that satellite M arises from the second neighbour. Stakelon has observed several of these satellites in single crystals of CuFe. His earlier work on single crystals of CuCo has enabled him to prove that one of the satellites there arose from the first neighbour. We have tentative evidence from his work that M has the angular dependence appropriate to a second neighbour. *Figure 2* is a plot of inverse of the splittings versus T. The straight lines are least squares fits to the data. Note that they fit straight lines and thus give a Curie–Weiss law. The values of T_K obtained are 29.2 $\pm$ 2.4 K for B, 27.6 $\pm$ 4.0 K for C, 29.2 $\pm$ 2.3 K for M and 29.3 $\pm$ 7.1 K for N. *Figure 3*

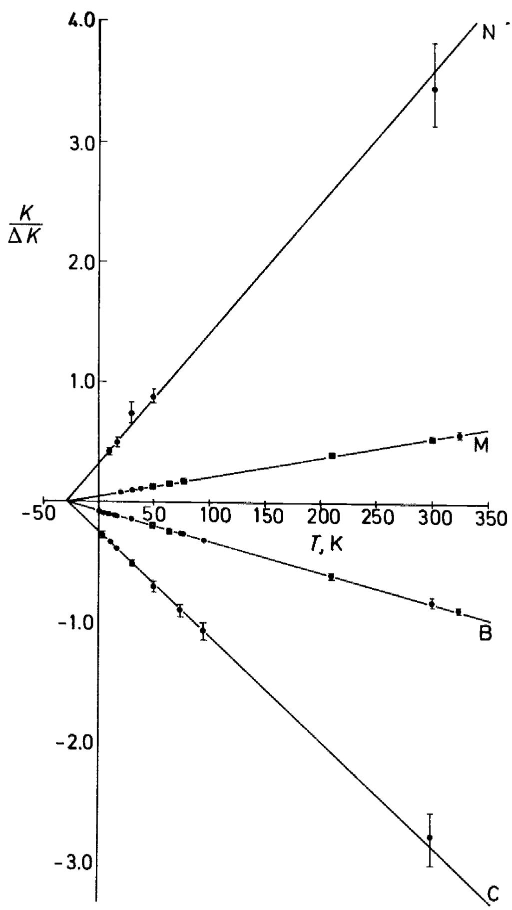

Figure 2. $K/\Delta K$ versus temperature for four of the satellites. The straight lines are least squares fits to the data

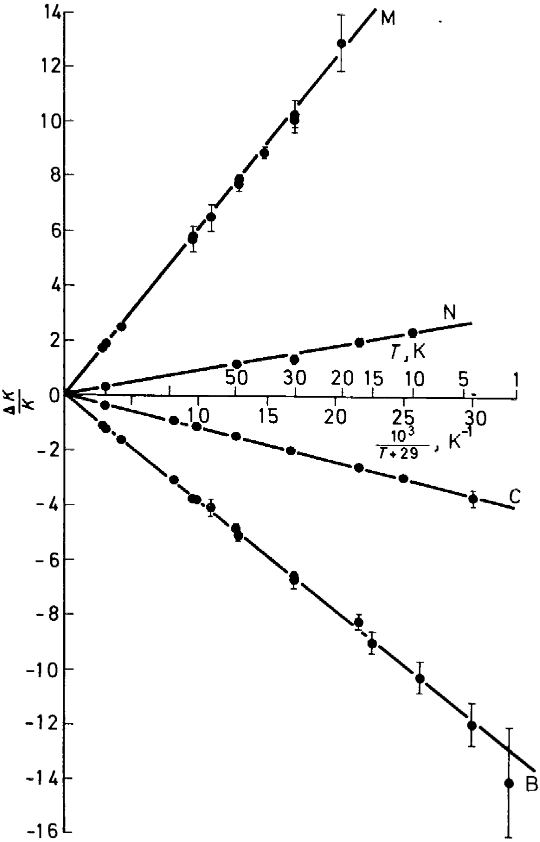

Figure 3. The Knight shifts versus $1/(T + 29)$ for four of the satellites. No additional polarization is seen to form below $T_K = 29$ K

shows the splittings themselves plotted versus $1/(T + 29)$. These are seen to be straight lines. This form of plot emphasizes the low-temperature points. Bearing in mind that the Kondo temperature is 29 K from magnetic susceptibility experiments, we see that the spin polarization has the same temperature dependence. We thus are able to distinguish between the two proposed forms and conclude that equation (1) correctly describes the form of the spin polarization. That is to say, the entire temperature dependence is given by the magnetic susceptibility. The Kondo effect is responsible for the temperature dependence of the magnetic susceptibility, but apart from that there is no extra 'Kondo compensation' causing a spatial change with temperature.

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