PARAMAGNETIC RESONANCE TRANSMISSION IN COPPER-DILUTE MANGANESE ALLOYS*

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This Letter reports the observation of large electron paramagnetic resonance (epr) signals transmitted through "thick" foils of Cu-dilute Mn alloys. The signals are interpreted as arising from the combined resonance of the conduction electrons and the localized mangetic moments formed about the manganese ions, and provide direct evidence for a strong isotropic exchange coupling between these two systems.

Spin resonance from localized manganese moments in copper was first observed by Owen et al.,[1] who found a single, surprisingly narrow line with a nearly-free-electron g value of $g \approx 2.01$. Assuming the spin coupling between the ions and the 4s conduction electrons to be an S-d exchange of the form $H' = A\vec{S}\cdot\vec{s}$, they pointed out that the conduction electrons should provide a very potent relaxation mechanism for the manganese magnetization. With a plausible value for A in the neighborhood of 1 eV, the expected lifetime broadening $\gamma\Delta H \approx 1/T_2 \approx (A^2/E_F^2)(kT/\hbar)$ is about 10^2-10^3 G/°K, some two orders of magnitude greater than their observed linewidths.

As we recognized at the time, the above relaxation mechanism can only be fully effective if the conduction electrons are able to stay in thermal equilibrium with the lattice. Since the two kinds of spins have about the same electronic g factor, when the lattice coupling is very weak the magnetizations will precess together, maintaining their alignment, and in macroscopic terms the conduction electrons are unable to produce any torques on the ions. In this limit, the entire observed magnetization must relax through the weak conduction-electron–lattice coupling, and the effective relaxation time will be $1/T_{\text{eff}} = (1/T_e)\chi_e/(\chi_e + \chi_i)$, where T_e represents the contact between conduction electrons and lattice, and χ_i and χ_e are the ionic and Pauli susceptibilities, respectively. Since χ_i is usually much greater than χ_e, the relaxation is bottlenecked. Hasegawa[2] discussed this situation and solved a pair of coupled phenomenological equations of motion for the two magnetizations. He concluded, from the relatively limited data available, that the effect could be an important one in the Cu-Mn system.

We have performed several conventional epr experiments which give qualitative support to this idea, and which motivated the search for a transmission signal. These are, briefly, the following: (a) We have found no sign of the 300-G manganese hyperfine splitting[3] even at concentrations as low as 40 ppm. This makes it unlikely that the observed narrow line ($\approx$35 G) is due to a long-range ion-ion coupling of the Ruderman-Kittel-Yosida[4] type and suggests some dynamic effect. (b) Above 5-10°K the linewidth increases linearly with temperature, while the slope increases from $2\frac{1}{2}$ G/°K at 2% Mn to about 12 G/°K at 0.16% Mn. This is in the right direction for easing of a bottleneck by reducing the Mn susceptibility.[5] (c) Measurements of relative intensity versus concentration show an anomalous decrease in the signal at low concentrations, as would be expected if magnetization were being lost from the sample surface by diffusion out of the skin depth.[6]

These results are all in agreement with a model in which large transverse magnetizations of the ion system are preserved even in the presence of "flip-flop" collisions with the conduction electrons. An electron which has "exchanged spins" with a manganese ion is much more likely to undergo a second exchange with a different ion than to relax to the thermal reservoir. The primary role of the conduction electrons then is to redistribute the nonequilibrium ion magnetization through the metal. The electrons diffuse through the sample with diffusivity $D = \frac{1}{3}\Lambda v_F$ and will travel a distance $(D\tau)^{1/2}$ in time τ. Since they carry only a fraction $\chi_e/(\chi_e + \chi_i)$ of the total transverse magnetization, this total magnetization will diffuse with a characteristic length

$$\delta_e \approx \left[D\frac{\chi_e}{\chi_e + \chi_i}T_2\right]^{1/2}, \tag{1}$$

where $1/T_2 \approx \gamma\Delta H/1.5$ is the observed lifetime-limited linewidth. The addition of a diffusion term[7] to Hasegawa's equations of motion for the magnetizations, and simultaneous solution with Maxwell's equations, will give this result in the appropriate limit. At low manganese concentration, the conduction-electron mean free path Λ becomes large and δ_e can be much greater than a microwave skin depth. It should then be possible to perform selective transmission experiments,[8,9] a technique which has been exploited with great success in the study of conduction-electron spin resonance in pure metals.[10]

The experiment involves two TE_{101} rectangular microwave cavities with a common wall containing a $\frac{1}{2}$ cm^2 "window" of Cu-Mn foil. The cavities are immersed in liquid helium and one of them is tunable from outside the bath. The transmitter cavity is driven with the order of 20 mW of power from an automatic-frequency-control stabilized klystron operating at 9100 MHz. As the external magnetic field is swept through resonance, coherent transverse magnetization generated within the skin depth diffuses through the foil and radiates power into the receiver cavity. This power is modulated at 400 Hz with a microwave chopper and detected in a sensitive superheterodyne receiver with a 30-MHz i.f. Coherent detection at 30 MHz is followed by coherent detection at 400 Hz in the usual manner.

A typical transmission signal in a sample containing nominally 100 ppm of manganese is shown in Fig. 1(c). The foil thickness is 20 μ, which corresponds to around 100-microwave skin depths. (The sample is slightly into the anomalous skin-depth region.) Microwave phase shift has been arbitrarily introduced to give a symmetric signal. For purposes of comparison, Figs. 1(a) and 1(b) show signals taken by conventional reflection. In Fig. 1(a) we have the reflected (derivative) signal from an "empty" cavity, which shows a large background signal of unknown origin. This background was present in all reflection runs (with three different cavities) in spite of repeated cleaning. This would mask entirely the weak signal from the $\frac{1}{2}$-cm^2 sample of Fig. 1(c); so in Fig. 1(b) we present the reflected (derivative) signal obtained when the cavity contains about 20 cm^2 of stacked foils of sample.

The g value for the transmitted signal is $g = 2.011 \pm 0.005$, equal to that of the reflected signal and significantly removed from that of conduction electrons in pure copper, $g_e = 2.031 \pm 0.003$.[10] The total transmitted power of 10^{-14} W is about 6 dB above the nonresonant power which appears in the receiver cavity because of spurious leakage, and is over two orders of magnitude greater than conduction electrons alone could contribute.

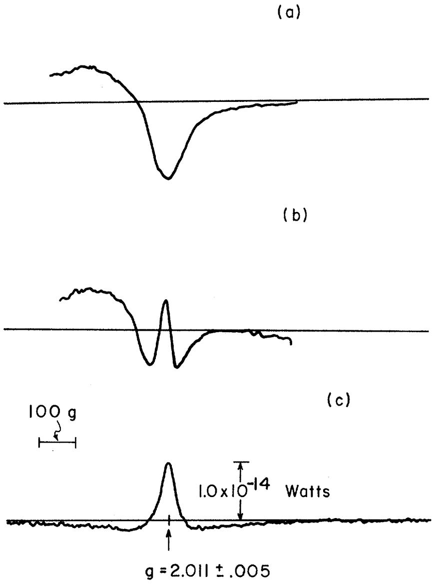

FIG. 1. Resonance traces at 1.5°K. (a) Derivative of the reflected signal in an unloaded cavity, showing the large background. (b) Derivative of the reflected signal with a cavity containing 20 cm^2 of 100-ppm Mn-Cu foil. (c) Direct transmitted signal through $\frac{1}{2}$ cm^2 of 100-ppm Mn-Cu foil with a thickness of 20 μ.

Figure 2 gives the amplitude of the transmitted signal as a function of sample thickness. The expected behavior would be a signal voltage proportional to $\exp(-t/\delta_e)$ with δ_e given by Eq. (1).[11] The Mn concentration in these nominal 100-ppm samples is a bit uncertain, since chemical analysis gave only 70 ppm and the measured resistivity ratio of 40 corresponds to about 130 ppm. Assuming 100 ppm, and using the free electron susceptibility for the conduction electrons, $(\chi_e + \chi_i)/\chi_e \approx 27$ at 1.5°K. This then yields $\delta_e \approx 7$ μ. Since both band-structure effects and many-body corrections should increase this number, the agreement with the measured value, $\delta_e = 10$ μ, is very reasonable. As a further check, the transmitted signal amplitude can be extrapolated back to zero thickness and compared with the reflection signal after correction for filling factor and derivative detection. The corrected reflection amplitude is plotted as a square at $t = 0$, and the agreement is quite good. Some data have been taken at 4.2°K, where the principal change is a substantial decrease in intensity due to the Curie susceptibility of the ions. The transmit-

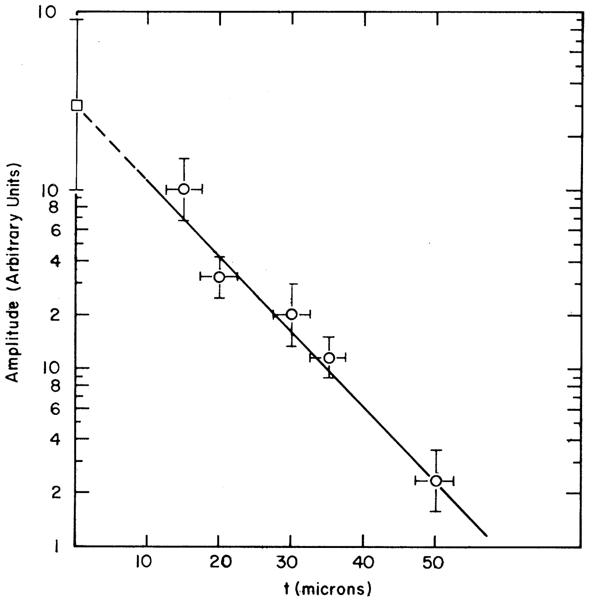

FIG. 2. Amplitude of the transmitted signal as a function of film thickness. The heavy line corresponds to exponential attenuation with a diffusion length of 10 μ. The dashed extrapolation allows a comparison with the adjusted reflection signal, which is plotted as a square at $t = 0$.

ted signal has also been observed in a 40-ppm alloy.

Even in the absence of diffusion, the anomalous-skin-depth modulation observed in Gd[12] and described by Hirst[13] and VanderVen[14] would lead to a resonant transmission of power in these samples. At these low concentrations, however, the antiresonance modulates the very small effective skin depth by only a few percent, and this contribution is negligible.

We conclude that the anomalous epr behavior of manganese-doped copper is due to a strong exchange coupling between the ions and conduction electrons, together with a weak electron-lattice coupling, as suggested by Hasegawa. In addition, the mobility of the electrons plays an important role. Similar effects are probably significant in some of the other metals which show epr of dissolved local moments. Selective transmission appears to be a useful and sensitive technique for investigating these systems.

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