NMR Studies of Spin-Glass Dynamics

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The dynamics of Mn impurities in dilute *Cu* Mn (12, 20, and 43 ppm) have been studied in the spin-glass regime, down to $\sim T_G/30$. In an applied field of 275 Oe, the spins freeze gradually although their motions are highly correlated below a well-defined temperature T_G, which is the same as that found in static susceptibility measurements. At T_G, no anomaly is found on the impurity correlation time τ_e, which is field dependent.

We report on NMR studies of the longitudinal relaxation of host nuclei in dilute *Cu*Mn alloys from above to far below the onset of the spin-glass regime. Measurements of T_1 yield information on the transverse fluctuating fields experienced by the nuclear spins at the Larmor frequency ω_n. In a dilute magnetic alloy these fields come primarily from the RKKY (Ruderman-Kittel-Kasuya-Yosida) hyperfine interactions. Their time behavior is linked to the dynamical properties of the impurities. The high-temperature regime where impurities behave as free spins has been studied by Alloul and Bernier[1]: The correlation time of paramagnetic Mn spins in *Cu*Mn is $\sim 10^{-11}/T$ sec. The work presented here has been performed in a temperature region where impurity interaction energies become comparalbe to or larger than $k_B T$. We have reached two conclusions: (1) There exists, even in sizable applied fields, a rather well-defined temperature T_G below which all impurities interact and behave collectively. This temperature corresponds to the static susceptibility ordering temperature. Impurity clustering appears gradually as the system is cooled down to T_G, becoming nearly complete at T_G. (2) The impurity spin dynamics slow down considerably when the temperature is swept through T_G but display no abrupt change. The observed behavior is typical of neither a well-defined cooperative transition[2] nor a glasslike freezing of thermally activated degrees of freedom.

Our host spin-lattice relaxation measurements have been performed on three dilute *Cu*Mn alloys of Mn concentration $C = 12$, 20, and 43 ppm. According to static susceptibility measurements,[3] these alloys order at 29, 44, and 87 mK, respectively. The temperature range of our NMR measurements extends from 2 to 300 mK on *Cu*Mn (43 ppm) at 310 kHz ($H_0 \sim 275$ Oe). Earlier measurements on all three alloys were performed from 25 mK to 2 K at 1.5 MHz ($H_0 \sim 1330$ Oe).[4] The shape of the copper nuclear magnetization recovery $M(t)$ is obtained by a series of $\pi/2$-$\pi/2$ sequences. Careful attention has been paid to heating effects at the lowest temperatures. The rotating rf field has an amplitude of 10 G; the receiver fully recovers from saturation in eight periods. There is no significant departure of the signal amplitude from Curie's law in the whole temperature range. The observed linewidth scales, as in previous work,[1,4] with the static magnetization.

The onset of interaction between impurities is reflected on the host NMR relaxation by two main features. First, we observe a progressive change of the magnetization recovery shape from an exponential form for $T \gg T_G$ to $\exp[a - (a^2 + t/\tau_n)^{1/2}]$ for $T \leq T_G$. This nonexponential low-T regime remains unchanged down to $T_G/5$. The second feature is a large enhancement of the impurity relaxation rate in the vicinity of T_G.

Over the whole temperature range, $M(t)$ has been found to follow the empirical equation

$$M(t) - M_0 = -M_0 \exp(-t/T_1^{K})\{A \exp(-t/T_1^{imp}) + (1-A)\exp[a - (a^2 + t/\tau_n)^{1/2}]\}. \quad (1)$$

The Korringa relaxation time T_1^{K} ($1.27/T$ sec) is long in our temperature range and only yields a small correction. Parameters T_1^{imp}, τ_n, a, and A, are obtained by a computer fit of Eq. (1) to the experimental curves. The functional de-

pendence (1) of $M(t)$ is found to be accurate down to instrumental scatter (~0.3%). Parameter A represents the mixing of the high-temperature relaxation regime involving T_1^{imp},[1] and the low-temperature nonexponential regime. As seen in Fig. 1, A varies linearly with c/T above T_G and vanishes for $T<T_G$. Parameter A reflects the progressive appearance of interactions at temperatures well above T_G. It indicates the proportion of copper nuclei influenced by free impurities and may be regarded as a measure of the number of free spins. It is not affected by the magnetic field and scales in T/c. The breakpoint temperature of the plot of A vs c/T occurs, within experimental resolution, at the same temperature as for static susceptibility measurements.[3] The time scales of those two measurements span from ~1 sec to $1/\omega_n \sim 10^{-7}$ sec. The fact that the transitional feature is found at the same temperature in a wide time domain contradicts Murani's observation with neutrons on a concentrated *Cu*Mn alloy.[5]

In Fig. 2 we have plotted τ_n vs T over the whole temperature range in which nonexponentialities exist. The relaxation process becomes more effective in the vicinity of T_G and is maximum at $\sim T_G/2$. It is clearly established by this raw data that there is no abrupt freezing of impurity spins at T_G. We consider now the shapes of the recovery. A relaxation going as $\exp(-\sqrt{t/\tau})$ is, in some cases, characteristic of diffusionless processes.[6] This is not so in the present study. Although the relaxation rate becomes rather fast near T_G, it does not override the diffusion of magnetization. Indeed, the spin diffusion coefficient D (~5×10^{-13} cm^2/sec for Cu) is not likely to be significantly altered by the onset of interaction in the spin-glass state because the hyperfine fields are, for these low concentrations, comparable in magnitude to the nuclear dipole field: The diffusion barrier number will not exceed its high-field value of 3600.[1] Thus, even for the fastest τ_n, the nuclear magnetization diffuses over at least half of the host nuclei. The corresponding contribution to the magnetization recovery would be exponential. As this is not observed, we have to assume that the relaxation rate varies over distances of at least 50–100 Å in the sample. This assumption is justified by the two following facts: (1) The dynamics of impurity spins depend on local environment and so vary from Mn sites to Mn sites. (2) The length over which the magnetization diffuses during the recovery, $\lambda \sim \sqrt{D\tau_n}$, is, in our experiment, of the order of the mean distance between impurities. So, the diffusion process, although not blocked as already stated, is not efficient enough over large distances to cancel host magnetization difference between various impurity spheres of influence. In each sphere, rapid diffusion prevails. The spheres of influence are independent of one another. The spin-lattice relaxation recovery shape, observed below T_G, results from the superposition of exponential recoveries about each impurity. The macroscopic nuclear magnetization at time t is expressed by

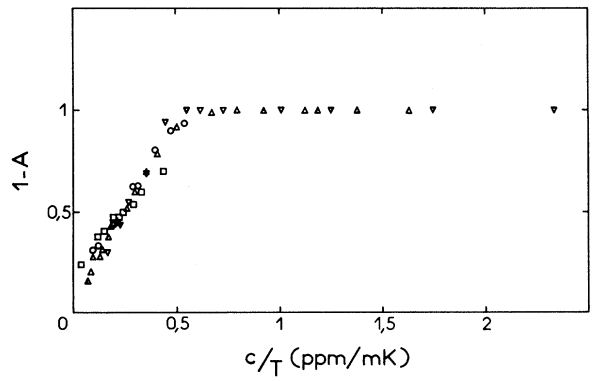

FIG. 1. Mixing parameter $1-A$ plotted vs c/T, with c in ppm, and T in mK for 12 (□), 20 (○), and 43 ppm (Δ at 1.5 MHz, ∇ at 310 kHz). This parameter $1-A$ represents the fraction of correlated impurities.

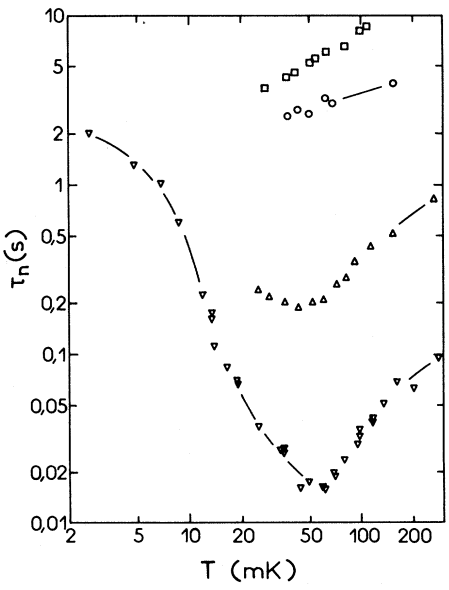

FIG. 2. τ_n vs temperature as given by Eq. (1). τ_n is a mean nuclear relaxation time. □, ○, Δ: 12, 20, and 43 ppm, respectively, at 1.5 MHz; ∇, 43 ppm at 310 kHz.

$$M(t) = M_0[1 - \exp(-t/T_1^{K}) \int_0^{\infty} P(T_1^{loc}) \exp(-t/T_1^{loc}) dT_1^{loc}], \quad (2)$$

where $P(T_1^{loc})$ is the distribution function of local relaxation times T_1^{loc} and is obtained from Eq. (1) by an inverse Laplace transform:

$$P(T_1^{loc}) = 2(\pi \tau_n T_1^{loc})^{-1/2} \exp(a - a^2 \tau_n / T_1^{loc} + T_1^{loc}/4\tau_n). \quad (3)$$

Parameter a has a nearly constant value of 0.3 for all samples. The probability distribution $P(T_1^{loc})$ has a broad maximum in the vicinity of τ_n and falls off exponentially far below and far above.

Within this phenomenological framework, we now extract information about the impurity spin dynamics in the same way as done by Alloul and Bernier[1] in the high-temperature regime. However, the spin-glass state differs from the paramagnetic state in two respects: (1) a given impurity spin tends to align along a preferential direction, which is oriented at random if the applied field is low compared to $H_L \sim k_B T_G / g\mu_B$. The resulting angular distribution causes a mixing of the longitudinal and transverse localized electron spin suceptibilities inducing the host nuclei relaxation. The BGS (Benoit—de Gennes—Silhouette) mechanism, which is known[1] to be responsible for the high-temperature relaxation, is enhanced by a factor which may be as large as $(\omega_e/\omega_n)^2 = (g\mu_B/\gamma_n)^2$. (2) Short-range correlations are likely to sustain local, quasipersistent spin-fluctuation modes which are at frequencies low compared to the RKKY coupling $[(\gamma_n H_L)^{-1} \sim 10^{-6}$ sec for 43 ppm] and may eventually become well-defined spin waves at long wavelength. In spite of these complications we shall describe the slow fluctuations with a simple Lorentzian spectrum $\tau_e/[1+(\omega\tau_e)^2]$, the virtue of which is to characterize the impurity spin dynamics with one parameter only. We expect a distribution $P(\tau_e)$ over impurity sites of the correlation time τ_e. The distribution $P(\tau_e)$ will stem from $P(T_1^{loc})$, given by Eq. (3), once the relaxation mechanism has been identified and worked out quantitatively. At present, we can give the gross features of a mean τ_e corresponding to τ_n through the following reasoning. In Fig. 2, τ_n vs T displays a minimum at about $T_G/2$, which, from the preceding discussion, is assumed to correspond to $\omega_n \tau_e \sim 1$. For the 43-ppm sample, $\tau_e \sim 10^{-7}$ sec at 1.5 MHz and $\sim 5 \times 10^{-7}$ sec at 310 kHz. The temperature dependence of this mean impurity correlation time is obtained from the relation $\tau_n^{-1} \propto \tau_e/[1+(\omega_n\tau_e)^2]$ and is shown in Fig. 3. The variation of τ_e vs T is smooth through T_G and goes as T^{-2} for the lower applied field. Impurity dynamics are clearly affected by external magnetic fields—the smaller the field, the slower the fluctuations. The present study cannot bring any definitive clue as to zero-field dynamics, the applied fields being much larger than the blocking fields of the antiferromagnetic domains (or clouds) which are known, from remanence effects, to exist in spin-glasses below T_G.[7]

The transition from a fast- to a slow-fluctuation regime has also been observed on the transverse relaxation time T_2 as measured in conventional pulsed NMR[8,9] or with muon-implantation techniques.[10] The NMR studies on higher concentration (0.2–1%) alloys of Refs. 8 and 9 agree qualitatively with our conclusions on spin dynamics but do not yield quantitative information on the sharpness of the transition. The onset of fast muon depolarization at T_G has been interpreted as an indication of the existence of a cooperative phenomenon at T_G.[2] Such a conclusion seems to us to be disputable as this fast depolarization can be caused, besides the slowing down

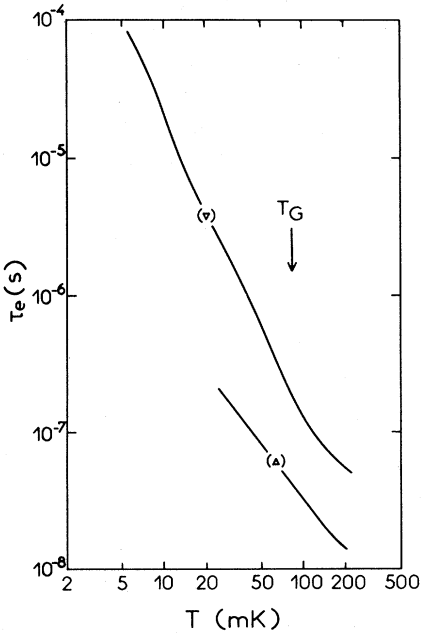

FIG. 3. Mean impurity correlation time τ_e vs temperature. ▽, 43 ppm at 310 kHz; ▽, 43 ppm at 1.5 MHz.

of spin dynamics, by the appearance of a spread in angles and magnitudes of the slow components of the local fields. Thus, experimental facts do not actually hint toward a usual kind of magnetic phase transition at T_G although the existence of a fairly well-defined, unique temperature at which all (or almost all) spins are correlated seems to be emerging from a host of different experiments, including EPR,[11] with the possible exception of neutron scattering with finite wave-vector transfer.[5]

A possible picture which comes to mind and accounts for the behavior of A is due to Smith[12] and it is that of small clusters forming above T_G and growing so as to become linked together at T_G. The proportion of clustered spins varies with temperature as shown in Fig. 1. The dynamical behavior of clustered spins is represented by an average fluctuation time τ_e in Fig. 3. However, the absence of transitional features on τ_e—that the dynamical properties of a given spin in a finite cluster slightly above T_G are little different from its behavior on the infinite cluster slightly below T_G—does not hint at the existence of a cooperative phenomenon at T_G.

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High-Frequency Behavior of "Ideal" Superconducting Point Contacts

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We have studied niobium point contacts which are very consistent and reproducible from junction to junction, in both their dc and high-frequency behavior. We find a strong correlation between the sharpness of the gap structure and the ac Josephson effect, and we present the first quantitative measurements of the far-infrared frequency dependence of the Josephson effect above the energy gap. The measured I-V curves are also compared with available theoretical models.

Of all the types of superconducting weak links that exhibit the ac Josephson effect, niobium cat-whisker point contacts[1] have the best high-frequency performance, and have shown direct evidence of the ac Josephson effect up to about 6 times the energy-gap voltage.[2] Their very small area minimizes the shunt capacitance,[1] while their three-dimensional geometry and high resistance minimize the effects of heating,[3] making them the best type of weak link for a study of the behavior of the ac Josephson effect at high frequencies. Unfortunately, the dc I-V curves and high-frequency behavior can vary considerably from junction to junction. We have conducted a systematic study of cat-whisker point contacts and have correlated the high-frequency behavior and the characteristics on the dc I-V curves of the various types of junctions commonly obtained. We find that those junctions with the best high-frequency performance have both a shape of dc I-V curve[4] and a high-frequency behavior[5] that are consistent and reproducible from contact to

