For noninteracting impurities, the theory has been used to predict the weight of the central peak with the following result:

$$\chi(q) = \int S(q, \omega)\, d\omega = c(x_n/x_d)^2 J_0^2 \chi_s^2, \quad (1)$$

which has been expressed in terms of the parameters of the pure system and the isolated impurity. Here $x_n$ and $x_d$ represent the linearized mean-field response of a normal (potassium) and a defect (lithium) site to its surroundings, and $J_0$ describes the nearest-neighbor interaction. Since $x_n$, $x_d$, and $J_0$ are model parameters independent of experimental conditions, Eq. (1) predicts that $\chi(q)/c\chi_s^2 = \text{const}$ for all concentrations $c$ and temperatures. We show in Fig. 4(b) that for $\chi(q)$ and $c$ varying over one and one-half orders of magnitude, $\chi(q)/c\chi_s^2$ varies by less than a factor of 2. This shows clearly that mean-field theory predicts reasonably well the weight of the central peak for noninteracting impurities. At concentrations above 8%, $\chi(q)/c\chi_s^2$ drops drastically to about 1/100 of its low-concentration value at a lithium content of 24%. In this concentration range the Cole-Cole plots become flattened and are indicative of an entire (nonlognormal) spectrum of hopping frequencies which are responsible for dielectric relaxation. This should give rise to a broadening of the central peak—an effect which might be resolved by neutron scattering. At a lithium concentration of 40%, the coupled Li modes apparently become soft, driving the crystal into a complicated ferroelectric structure of the tungsten-bronze type.[11]

The present results have shown that Li is an impurity which, when incorporated in the $KTaO_3$ host at concentrations below ~1%, is responsible for an extremely narrow (1 kHz) central peak. Its dynamic properties are correctly described by mean-field dynamics of a static impurity in a ferroelectric host. At higher concentrations the central peak is broadened and, above ~25 K, the transition between static and dynamic behavior occurs. $KTaO_3$:Li does not become ferroelectric at any temperature as long as the lithium concentration is less than 24% and the observed dielectric dispersion cannot be identified with a ferroelectric soft mode.

We acknowledge illuminating discussions with E. Courtens and K. A. Müller. Oak Ridge National Laboratory is operated by Union Carbide Corporation under Contract No. W-7405-Eng-26 with the U. S. Department of Energy.

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## Spin-Flip Scattering Time of a Spin-Glass

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We have used, for the first time, superconducting tunneling to study the magnetic ordering properties of a normal metal. We find that the spin-flip scattering time of a spin-glass increases markedly as the temperature is lowered through the temperature at which the susceptibility exhibits a cusp. The results are interpreted as a measurement of the temperature dependence of the spin-glass order parameter.

In order to elucidate the character of the spin-glass phase transition, we have undertaken extensive measurements of the temperature dependence of the conduction-electron spin-flip scattering time of AgMn, through the ordering temperature $T_G$, using an electron tunneling technique. We

find that the spin-flip cross section is roughly constant above $T_G$, suffers a drop by ~5% in the vicinity of $T_G$, and then remains constant to lower temperature.

Spin-glasses[1] are systems that involve magnetic impurities in the percentage range distributed randomly in a host noble metal, with AgMn serving as an archetype. One of the most fundamental microscopic quantities that characterizes a magnetic phase transition in a metal is the spin-flip scattering time of the conduction electrons off of the correlated local spins. The spin-flip cross section can be directly related to the localized instantaneous spin-spin correlation function. The most sensitive way of measuring the spin-flip scattering time is using superconductivity as a probe. The density of states near the Fermi surface, for gapless superconductors with magnetic impurities, provides a direct measure of the spin-flip scattering time.[2] To study the properties of normal (i.e., nonsuperconducting) magnetic metals, we use the proximity effect to induce superconductivity. We then measure the density of states by tunneling into the normal metal. This technique has been used earlier to study the Kondo effect in dilute magnetic alloys.[3]

Approximately two hundred proximity-effect tunnel junctions were prepared and measured. The junctions were of the form $N$(1000–3000 Å)-$I$-AgMn(200–800 Å)/Pb(3000 Å), where $N$ (a normal metal is Al, $Al_{0.95}Mn_{0.05}$, or Mg, and $I$ (an insulator) is $Al_2O_3$ or MgO thermally grown (1–2 h) in a humid oven at 100°C. A layer of ~700 Å of $SiO_2$ was evaporated, prior to oxidation, to mask the junction edges. The junction area was approximately 1 $mm^2$ and normal-state resistances ranged from 1 to 1000 Ω. After oxidation the films were replaced in the evaporator and pumped to the lowest pressure available (~ $8 \times 10^{-7}$ Torr).

AgMn was chosen as the archetype spin-glass because of the simple metallurgy of this alloy[4] and the ease with which proximity-effect junctions can be formed with it. Previous work[5] as well as our own microprobe analysis has shown that this system does not exhibit physical clustering. Our magnetic susceptibility studies on films[6] are in excellent agreement with the measurements on bulk samples, showing that AgMn is a "good" thin-film spin-glass system. The AgMn was induction-furnace melted and electron-beam-gun evaporated at a rate of 50 Å/sec. On each glass substrate, five tunnel junctions of varying thicknesses, but equal Mn concentrations, were formed. The evaporation procedure was standardized and kept the same as reported earlier.[6] Our previous magnetic susceptibility measurements[7] show that in this fashion the Mn concentration is ~15% of the concentration of the melt. The final Pb layer was deposited within 1–2 sec after the completion of the AgMn film.

The samples were cooled to nitrogen temperatures within a half-hour of evaporation, although some samples that were kept at room temperature for several weeks and then remeasured did not show an appreciable difference. Measurements were performed in $He^4$ as well as in a dilution refrigerator. Some samples were subjected to a maximum field of 40 kG in a search for remanent effects, which were not observed.[8] The tunneling curves were measured using a standard tunneling bridge and the temperature was measured and/or controlled using a Ge or Si diode temperature sensor. The usual Rowell tests[9] were run to test the quality of the junctions.

Figure 1 shows a comparison of the normalized conductance of a $N$-$I$-AgMn(200 Å)/Pb(3000 Å) with 0.5-at.% Mn concentration tunnel junction, a $N$-$I$-Ag(200 Å)/Pb(3000 Å) junction in 859 G ($H/H_{c3}$ ~0.91) adjusted for the same gaplessness (same zero-bias concuctance) as the AgMn sample and the prediction of Abrikosov and Gor'kov (AG).[10] The AgMn/Pb sample shows a pronounced peak at

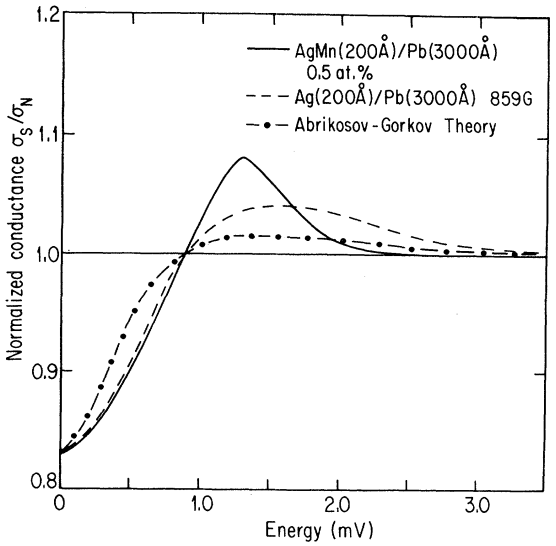


FIG. 1. Comparison of the normalized conductances of a sample of AgMn, an Ag sample driven gapless by a parallel magnetic field both at 1.10 K and the AG theory. Notice the disagreement of the experiments with the AG theory.

voltages below the peak in the Pb density of states. The Ag/Pb sample in a magnetic field is less peaked and closer to the AG prediction. This behavior is qualitatively in agreement with the McMillan model,[11] which suggests that the density of states in the normal metal ($N$) is increased in the voltage region where the density of states in the superconductor ($S$) is decreased and vice versa. For the AgMn sample the pair breaking occurs in $N$ so that the conductance is larger below the Pb gap. For the Ag sample in the surface superconductivity regime, the pair breaking occurs predominantly within the Pb film. Consequently there are states in the $S$ film below the Pb gap and this reduces the density of states in the $N$ film. It should be pointed out that neither of the samples agrees well with the AG theory. We also compared our data with the Kaiser-Zuckerman theory[12] and find quite marked qualitative differences.[13]

The zero-bias conductance of a tunnel junction provides a direct measure of the density of states at the Fermi surface. In a superconductor containing magnetic impurities in sufficient concentration to cause gaplessness, the zero-bias conductance is strongly dependent upon the spin-flip scattering time. In a proximity-effect sandwich the zero-bias conductance is even more sensitive to the spin-flip scattering. The magnetic impurities attenuate the order-parameter penetration into the normal metal and also produce a depairing field which, when compared with the local order parameter, results in increased gaplessness. The temperature dependence of the zero-bias conductance below ~3.5 K is due to a change in the spin-flip scattering and due to thermal smearing of the density of states $N(E)$. The zero-bias conductance is given by

$$\sigma_s(0) \propto \int_{-\infty}^{\infty} N(E) \frac{\partial f}{\partial E} dE, \qquad (1)$$

where $f(E)$ is the Fermi function. The finite width of the derivative of the Fermi function smears the density of states. The Pb gap function is saturated below ~3.5 K and it contributes to the temperature dependence only above this temperature.

In order to compare our data with simple thermal smearing, we measured the density of states between 0.040 and 8 K for a $N$-$I$-AgMn(400–600 Å)/Pb(3000 Å) sample with 0.35-at.% Mn concentration. The 40-mK density of states then was used as a zero-temperature density of states to numerically compute the temperature evolution of $\sigma_s(0)$ from Eq. (1). A comparison of the calculated and measured zero-bias conductances is shown in Fig. 2. The existence of strong pair breaking in these samples is proven by the fact that similar samples of 400-Å Ag thickness with no Mn impurities have a normalized zero-bias conductance of ~0.1 as opposed to >0.94 in the present samples. For a gapless superconductor the zero-bias conductance is expected[2] to be

$$\sigma_s(0) \propto N_s(0) \simeq N(0)[1 - \tfrac{1}{2}(\Delta\tau_s)^2], \qquad (2)$$

where $N(0)$ is the density of states at the Fermi surface in the normal state, $\Delta$ is the order parameter at the oxide layer, and $\tau_s$ is the spin-flip scattering time. For samples with the same normal-metal thickness our concentration studies exhibit approximately the dependence in Eq. (2), in the strongly gapless regime.

Figure 2 shows that the calculated curve follows the experimental data and then deviates in the region around $T_G$ as determined from static susceptibility data.[5] The difference between the computed and experimental curves, $\delta\sigma$, is a measure of the temperature-dependent part of the spin-flip scattering time for electrons near the Fermi surface. Note that the two curves for different thicknesses deviate at the same temperature, indicating that this is an intrinsic effect of the spin-glass and not a property of the proximity effect. The fact that the computed curve falls

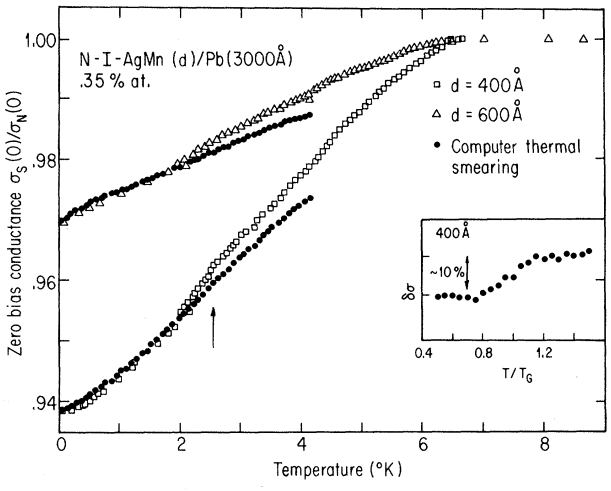


FIG. 2. Normalized zero-bias conductance as a function of temperature for two thicknesses of AgMn samples with 0.35-at.% Mn concentration. The full circles show the computed thermal smearing of the 40-mK data. The difference between experiment and computer calculation, $\delta\sigma$, shown in the inset can be related to $\tau_s$ as described in the text. (Within experimental error, $\delta\sigma$ is zero below $T_G$.)

below the measured one means that the spin-flip scattering time increases below $T_G$ in accordance with the idea that a degree of "spin-freezing" occurs at $T_G$. We wish to emphasize that this is manifesting itself as a gradual "step" and not a "cusp," as shown in the inset. It should be pointed out that the change in the spin-flip scattering time shows up as an ~10% change in the temperature-dependent part of the zero-bias conductance. Using Eq. (2) this corresponds to an ~5% change in $\tau_s$ across $T_c$, with the assumption that $\Delta$ is constant below 3.5 K. We note also that the step shape is consistent with the lack of $\vec{k}$ dependence in the spin-spin correlation function.[14]

Measurements for a *N-I*-AgMn(800 Å)/Pb(3000 Å) sample with 0.1-at.% Mn concentration are shown in Fig. 3. Note that the temperature at which the experimental and computed curves deviate has shifted to a lower temperature in proportion to $T_G$. A more-detailed concentration-dependence study will be given in a forthcoming paper.[13]

A simple second-order perturbation-theory calculation[15] shows that the spin-flip scattering time for a macroscopically condensed system is related to the autocorrelation function by

$$\frac{1}{\tau_s} \sim \frac{v_c}{\pi}\frac{m^2}{\hbar^5}\frac{1}{N}\sum_{\vec{k}}|I_{\vec{k}}|^2\frac{1}{|\vec{k}|}\int\frac{d\omega}{2\pi}\,g_{\vec{k}}(\omega)k_B T_c\,, \quad (3)$$

where

$$g_{\vec{k}}(t) = \overline{\vec{S}_{\vec{k}}(t)\cdot\vec{S}_{-\vec{k}}(0)} - \bar{\vec{S}}_{\vec{k}}\cdot\bar{\vec{S}}_{-\vec{k}} \quad (4)$$

(bars indicate thermal average), $T_c$ is the magnetic ordering temperature, $v_c$ is the unit-cell volume, and $I_k$ is the Fourier transform of the $s$-$d$ exchange integral.[15] After the integrations, the principal contribution can be shown to arise from the equal-time correlation function. This is a consequence of the rapid conduction-electron motion across the unit cell. Under such conditions, (3) and (4) combine to yield[15]

$$\frac{1}{\tau_s} \propto \sum_j \frac{1}{k_F^2}\int k\,dk\exp(i\vec{k}\cdot\vec{R}_j)(\overline{\vec{S}_j\cdot\vec{S}_0} - \bar{\vec{S}}_j\cdot\bar{\vec{S}}_0), \quad (5)$$

where $j$ and 0 are spatial indices.

For the model of a completely random spin-glass (neglecting short-range ferromagnetic correlations or the large $\vec{k}$ correlations implicit in the Ruderman-Kittel-Kasuya-Yosida interaction) the scattering rate per site is, by analogy,

$$1/\tau_s \propto \tfrac{1}{3}S(S+1) - \langle(\bar{S}_0)^2\rangle \quad (6)$$

(the brackets refer to configurational average). The last term in this expression is the order parameter defined by Edwards and Anderson.[16] In arriving at (6) we are making the assumption that only fluctuations in the spin-spin correlations result in conduction-electron spin flips. This is equivalent to the condition that the order parameter *cannot* flip the conduction-electron spins. We do not have a rigorous proof for such a condition but we believe it to be reasonable physically. The importance of the last term in (6) is that it leads directly to the remarkable conclusions that a measurement of the temperature dependence of the spin-flip scattering time is a direct measure of the temperature dependence of the spin-glass Edwards-Anderson–like order parameter.[17] The fact that only a 5% change is observed is not inconsistent with the relatively small change in the magnetic susceptibility below $T_G$.

In conclusion, we have used, for the first time, superconducting tunneling to probe the magnetic ordering properties of a normal metal. The spin-flip scattering time of a spin-glass (AgMn) is shown to have a step across the transition temperature, confirming the idea that spin freezing occurs below $T_G$. We identify the temperature dependence of the spin-flip scattering time as the temperature dependence of the spin-glass order parameter.

We would like to acknowledge useful conversations with S. Alexander, T. Holstein, P. Pincus, and P. Riseborough. We would like to thank E. P. Chock for preparing the master alloys, W. W. Fuller for performing some of the low-temperature measurements, and R. C. Dynes of Bell Laboratories for performing Rutherford back-

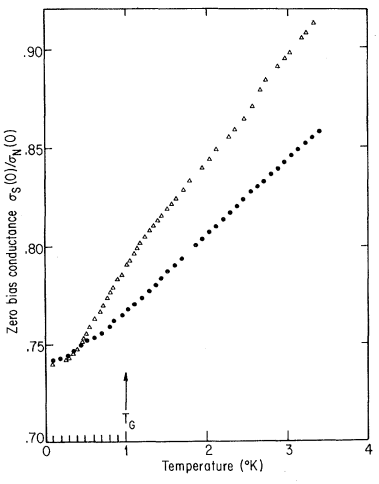


FIG. 3. Normalized zero-bias conductance as a function of temperature for an 800-Å AgMn sample with 0.1-at.% Mn concentration.

scattering on our samples. This work was supported in part by the U. S. Office of Naval Research Contract No. N00014-75-C-0245 and by the National Science Foundation Grants Nos. DMR 76-82347 and DMR 76-08899. One of us (P.M.C.) would like to acknowledge receipt of an Alfred P. Sloan Foundation Fellowship.

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# Magnetic Spin Susceptibility of $AsF_5$-Intercalated Graphite: Determination of the Density of States at the Fermi Energy

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The Schumacher-Slichter technique was utilized to determine the absolute Pauli spin susceptibility of stage-1 and stage-2 graphite-$AsF_5$ intercalation compounds. The results lead to a determination of the densities of states at the Fermi energy, $2.8\times10^{21}$ and $3.7\times10^{21}$ states/eV cm$^3$, respectively; substantially lower than in metals with comparable conductivity.

A wide variety of atomic and molecular species may be intercalated between the hexagonal carbon monolayers of graphite.[1] Because of the semimetallic character of pure graphite and the weak interplanar interactions, anisotropic metals with high basal-plane conductivities have been produced by intercalation of both electron donors (e.g., alkali metals) and acceptors (e.g., $HNO_3$, halogens, $AsF_5$). The acceptor compounds have yielded particularly high basal-plane conductivities and anisotropies, with the room-temperature $\sigma_a$ for $AsF_5$-intercalated graphite approaching that of copper.[2]

As summarized in Table I, experimental evidence suggests a relatively low carrier density resulting from partial electron transfer from the