Spinlike Susceptibility of Metallic and Insulating Thin Films at Low Temperature

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Susceptibility measurements of patterned thin films at sub-K temperatures were carried out using a scanning SQUID microscope that can resolve signals corresponding to a few hundred Bohr magnetons. Several metallic and insulating thin films, even oxide-free Au films, show a paramagnetic response with a temperature dependence that indicates unpaired spins as the origin. The observed response exhibits a measurable out-of-phase component, which implies that these spins will create $1/f$-like magnetic noise. The measured spin density is consistent with recent explanations of low frequency flux noise in SQUIDs and superconducting qubits in terms of spin fluctuations, and suggests that such unexpected spins may be even more ubiquitous than already indicated by earlier measurements. Our measurements set several constraints on the nature of these spins.

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The origin of $1/f^{\alpha}$ noise in superconducting quantum interference devices (SQUIDs) has been an unresolved mystery for more than two decades. Part of this noise of typically a few $\mu\Phi_0/\sqrt{\mathrm{Hz}}$ at 1 Hz appears to be surprisingly universal and behaves in every respect like true flux noise [1,2]. Measurements of electron spin dephasing rates of donors in Si also give evidence for magnetic noise originating at or near the surface [3]. Recently, evidence that a similar noise causes dephasing in superconducting qubits [4–7] has increased the interest in this phenomenon. Koch, DiVincenzo, and Clarke showed that fluctuating electron spins could explain the observed magnitude of noise [8]. Measurements of a flux offset in SQUIDs proportional to $1/T$ [9] provide direct evidence for the presence of spins in superconducting devices. Even though they are likely related to material imperfections such as surface oxides, defect states, or contaminations, the nature of these hypothetical spins is interesting for its own sake, and mitigating their effects is essential for several solid-state approaches to quantum computation. It is important to understand their origin and polarization dynamics, which determine the magnetic noise spectrum.

Various models assuming different relaxation mechanisms of unpaired electron spins on defects were recently proposed. Koch, DiVincenzo, and Clarke argued that the spin of an electron in a charge trap could remain locked until it leaves the trap [8]. A different model exploring thermally activated, nonmagnetic two level systems as cause for spin flips was motivated by the argument that only a small fraction of all defects have an activation energy low enough to allow charge fluctuations [10]. Faoro and Ioffe explored noise from spin diffusion mediated by RKKY coupling via the conduction electrons in metallic device elements [11].

We have measured the magnetic response of metallic and insulating thin films from $T = 25$ mK to 0.6 K, using a SQUID susceptometer in a scanning microscope. The most prominent result is a surprisingly large paramagnetic susceptibility with a $1/T$-like temperature dependence, and a magnitude consistent with a spin-1/2 density of about $4 \times 10^{17}/\mathrm{m}^2$, close to estimates from $1/f^{\alpha}$ noise levels in SQUIDs. Furthermore, the response has a measurable out-of-phase component, which implies polarization noise through the fluctuation-dissipation theorem. Our results thus demonstrate the existence of paramagnetic spins, with a density and dynamics suitable for producing $1/f^{\alpha}$ noise. Similar susceptibilities seen for Ag films and Au films with and without a sticking layer, together with previous results inferring the presence of spins in superconducting devices, suggest that the spins can occur similarly for different materials.

We focus on results from two samples, which were designed for other experiments [12] and include a range of structures with different layer combinations. On sample I, rings and wires were e-beam evaporated at a rate of about 1.2 nm/s from a 6N purity Au source onto a Si substrate with a native oxide [Figs. 1(f) and 1(i)]. First, the wires, with widths of 2 and 15 μm, were patterned using optical lithography and lift-off. Their thickness was 100 nm, including a 7 nm Ti adhesion layer. Subsequently, the micron-scale, 140 nm thick Au rings, which did not include any adhesion layer, were defined using e-beam lithography with PMMA [poly(methyl methacrylate)] resist and lift-off. Some of them were connected to the wider wires for heat sinking. Finally, Al rings for calibration purposes were fabricated in a similar way. Before each metal deposition, the developed resist was descummed in an oxygen plasma. The base pressure of our evaporator, which has never been used for magnetic materials, was below 5×10^{-7} Torr. On sample II, the first layer, an e-beam defined, 80 nm thick Au wire grid and bonding pads, was evaporated onto a Si substrate with native oxide

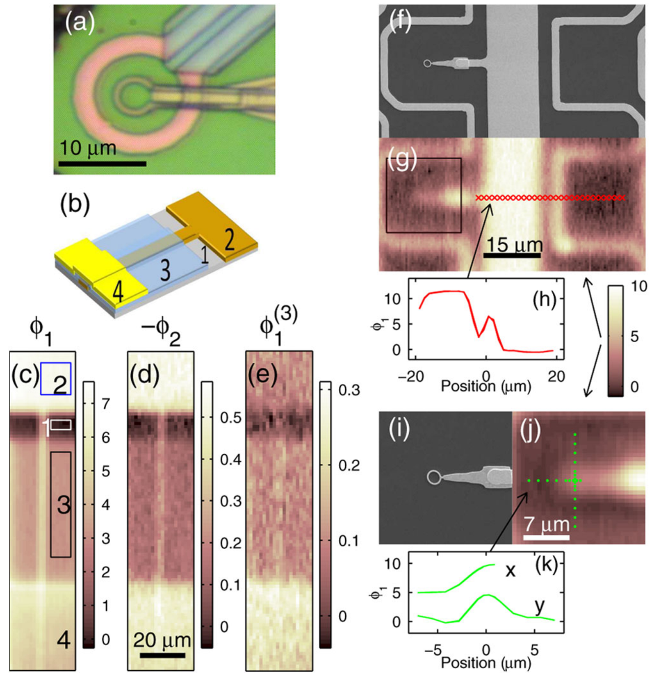

FIG. 1 (color online). (a) SQUID field coil and pickup loop. (b) Schematic of the layer structure of sample II: 1, bare Si; 2, Au with Al adhesion layer; 3, ALD deposited AlO_x; 4, Au on AlO_x. (c)–(e) Sample II, linear in- and out-of phase signal (ϕ_1, $-\phi_2$) and in-phase 3rd harmonic ($\phi_1^{(3)}$) at 193 Hz, 43 mK. All numbers in this figure are in units of $\mu\Phi_0$/mA and the response over bare Si has been defined as 0. (f) Scanning electron micrograph of a region of sample I, Au films on Si with native oxide. (g) Sample I: linear in-phase signal (ϕ_1) at 193 Hz, 27 mK of a region as shown in (f). (h) Line scans over the positions indicated in (g), at 25 mK and 111 Hz. Panels (i)–(k) are the same as (f)–(h), zoomed in on ring as indicated by the box in (g). The ring has a 2 μm diameter, 350 nm linewidth, and a connection to the 15 μm wide wire for heat sinking. The line scans in (k) were taken at 35 mK and the x scan is offset for clarity. The temperature dependence shown in Figs. 2(a) and 2(b) was obtained from line scans as in (h) and (k), or by averaging over the rectangles in (c).

from a source with unknown purity on top of a 1 nm Al wetting layer. A 50 nm thick AlO_x film, patterned using optical lithography and lift-off, was then deposited by atomic layer deposition (ALD). Rings and heat sinks similar to those on sample I were fabricated on top of the AlO_x [Fig. 1(b)], also without an adhesion layer.

Our dilution-refrigerator based microscope [13] employs SQUIDs [14] with an integrated 14 μm mean diameter field coil that is concentric with a 4.6 μm pickup loop [Fig. 1(a)]. These loops can be brought to within about 1 μm of the sample surface. The field coil applies an ac field H_a (35 G amplitude at its axis for most of the data discussed here, corresponding to a field coil current I_{FC} = 35 mA) to the sample, whose response couples a flux Φ_{SQUID} into the pickup loop. A second, counterwound pair of coils, located farther from the sample, cancels the response of the SQUID to the applied field to within one part in 10^4 [14]. As the field coil current varies sinusoidally in time (with amplitude I_{FC}), the SQUID response Φ_{SQUID} is conveniently characterized in terms of its complex nth harmonics, $\Phi^{(n)}$. We define $\phi_1^{(n)} + i\phi_2^{(n)} \equiv \Phi^{(n)}/I_{FC}$ and abbreviate $\phi_{1,2} \equiv \phi_{1,2}^{(1)}$. ϕ_1 and ϕ_2 quantify the in-phase and out-of-phase linear response, $\phi_1^{(3)}$ is proportional to the cubic component.

Figure 1 shows 2D susceptibility scans of both samples. For sample II, we took scans as shown in Figs. 1(c)–1(e) at a range of temperatures and extracted the temperature dependence [Figs. 2(a) and 2(b)] by averaging the indicated rectangular regions. For sample I, we averaged the complete $I_{FC} - \Phi_{SQUID}$ curves from many sinusoidal field

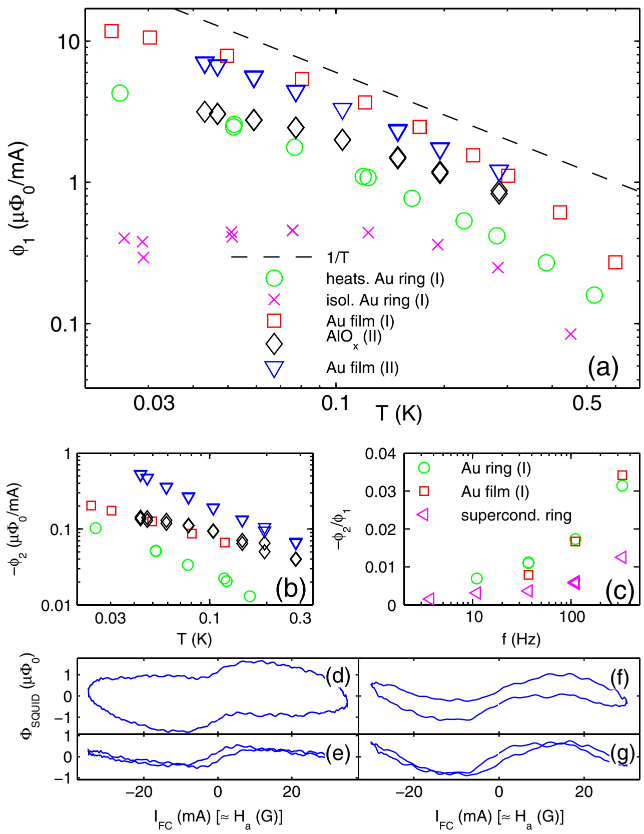

FIG. 2 (color online). (a) Temperature dependence of the in-phase linear susceptibilities (ϕ_1) obtained from scans as shown in Fig. 1 (see text) at 111 or 193 Hz. Numbers in parenthesis indicate the sample. The downturn at the highest T can be attributed to the T independent diamagnetic bulk susceptibility of -3.4×10^{-5} for gold [26]. (b) Out-of-phase component (ϕ_2) from the same data sets. (c) Frequency dependence of ϕ_2/ϕ_1 from sample I at 25 mK. The data from the superconducting ring characterize the phase shift due to the finite measurement bandwidth and show that the nonzero ϕ_2 is not a measurement artifact. (d),(f) Nonlinear part of the response of the heatsunk Au ring (I), deposited directly on the Si substrate, at base temperature. (f),(g) Same for an isolated ring on sample II, deposited onto the AlO_x film. In (d) and (f), only ϕ_1 (i.e., a line) was subtracted. In (e) and (g), both ϕ_1 and ϕ_2 (i.e., an ellipse) were subtracted.

sweeps at discrete positions as indicated in Figs. 1(g)–1(j). This procedure is more sensitive and allows us to determine the difference between the full responses including nonlinearities [Figs. 2(d)–2(g)] near and away from the metal. Figures 1(h) and 1(k) show ϕ_1 extracted from the response curves at each point. The T and frequency dependencies of the magnitude of the spatial variation along these line scans are included in Figs. 2(a)–2(c).

While the above measurements can detect only lateral *variations* of the sample response, the height dependence of the latter confirms that the observed signals reflect a response from the metal film. The height dependence over a third sample with a 1 μm thick SiO_x layer, grown at 1000 °C with a wet process, and above Si with only a native oxide give evidence for a paramagnetic $1/T$ surface response that is about a factor 5 and 30 smaller than that of the metal films, respectively [15]. The response from the ALD grown AlO_x film, which likely has a higher defect density than the thermal SiO_x, is comparable to that from the metal films [Fig. 2(a)]. Comparison with the value of ϕ_2/ϕ_1 for superconducting rings [Fig. 2(c)] shows that the nonzero value of ϕ_2 is not an instrumental artifact. Nevertheless, the actual sample contribution to ϕ_2 is somewhat smaller than the raw values displayed in Fig. 2(b) [15].

The $1/T$ dependence and the paramagnetic sign of the susceptibility $\chi(\omega) \equiv \chi_1 + i\chi_2$ indicate that it originates from localized spins. One can show that the z field emanating from a film of thickness d with an isotropic linear response is $\mathbf{B} = \mu_0 \chi d \partial \tilde{\mathbf{H}}/\partial z$, where $\tilde{\mathbf{H}}$ is the applied field reflected about the film (xy) plane. Using the measured pickup-loop-field-coil inductance and modeling $\tilde{\mathbf{H}}$ as the field of a thin loop leads to $\chi_{1,2} d = 8\ \mu\text{m} \cdot \text{mA}/\Phi_0 \cdot \phi_{1,2}$. For the films, this implies $\chi_1 T = 3 \times 10^{-5}$ K to within a factor of 2. We estimate systematic errors of less than a factor of 2 due to the simplicity of the model and uncertainties in the scan height. The response of the ring is consistent with this estimate within its somewhat larger calibration uncertainty. Comparing $\chi_1 T = 3 \times 10^{-5}$ K to the susceptibility $\chi_1 = \mu_0 n (g\mu_B)^2 J(J+1)/3k_B T$ of dilute spins with number density n and total angular momentum J leads to a concentration of 60 ppm for $d = 100$ nm, $g = 2$, and $J = 1/2$, corresponding to an area density of 4×10^{17} spins/m^2. Because all our films have a similar thickness, we cannot distinguish whether the spin density scales with the volume or surface area. For common magnetic ions with $g^2 J(J+1) \approx 35$ [16], the concentration would still be about 3 ppm, which is an order of magnitude larger than the specifications of our source material. For the materials investigated, the calculated equilibrium response from nuclear spins is several orders of magnitude smaller than the observed signals.

The magnetic moment noise spectral density from a sample of volume V and susceptibility χ that couples to a sensing loop as a dipole is $S_m(\omega) = -2k_B T \chi_2(\omega) V/\pi\omega$. This form of the fluctuation-dissipation theorem was verified for a spin glass, using a SQUID susceptometer similar to ours [17]. In our case, the expected magnetic noise from the sample is much too small to be detected directly. However, Ref. [8] shows that a spin density similar to our estimates can explain the observed $1/f^\alpha$ noise levels in SQUIDs. Integrating the dynamic susceptibility of fluctuating spins over the relaxation time distribution assumed in Ref. [8] leads to a value of ϕ_2/ϕ_1 that is also of the same order as our results. Although we cannot prove that ϕ_1 and ϕ_2 are of the same origin, the similar T dependence and consistency of the signs with a lag due to a finite relaxation rate do suggest a direct connection. While it is also not *a priori* clear to what extent our results apply to other metals including superconductors, the similar phenomenology of $1/f$ flux noise, our data from Au and Ag films and recent measurements on superconducting devices also showing a $1/T$ susceptibility component [9] indicate that all these effects are closely related.

The frequency dependence of χ_2 and the nonlinearities imply a millisecond-scale spin relaxation time for some spins, which indicates weak coupling to the conduction electrons. On the other hand, we find that the linear susceptibility of isolated metal rings saturates below approximately 150 mK [Fig. 2(a)]. In such rings, the electrons are expected not to cool below that temperature because of heating by Josephson oscillations in the SQUID [12]. This observation indicates that the spins thermalize with the electrons rather than the lattice, which suggests an electronic relaxation mechanism [18].

One may thus suspect a connection with evidence for spin impurities in metallic nanostructures and at surfaces and interfaces obtained from transport measurements. Enhancement of superconductivity in nanowires in an applied field indicates pair breaking by spins [19,20]. Weak localization measurements, which are a very sensitive probe for magnetic impurities [21], show that TiO_x adhesion layers for Au wires [22] and native oxides on Cu films [23] can cause spin-flip scattering. In contrast, our observation of similar susceptibilities from Au films with (wires sample I) and without Ti layer (rings I and II) shows that TiO_x is not the dominant source of spins in our samples. From standard weak localization measurements for $T \geq 300$ mK on wires fabricated together with the samples discussed above, we find a dephasing rate $1/\tau_\phi$ with a temperature dependence close to $1/\tau_\phi \propto T^{2/3}$, as expected for electron-electron interaction mediated dephasing [24]. The deviation from this power law behavior can be accounted for with 0.1 ppm of Mn impurities, if one allows the prefactor of the $T^{2/3}$ term to be a factor 6 larger than theoretically expected. In typical weak localization measurements, the discrepancy between the theoretical and experimental prefactor is no larger than a factor of 2 [21]. However, if the unusually large discrepancy in our case were due to spins, their Kondo temperature would have to be larger than about 1 K in order to explain the observed increase of τ_ϕ at low T. While we cannot rule out the existence of such spins, they cannot explain the susceptibility signal because their response would be quenched by the Kondo effect at low T. On the other hand, the measured $\tau_\phi \geq 1$ ns for $T \leq 1$ K sets a low upper bound on the spin-flip scattering rate and thus exchange coupling and Kondo temperature of the spins contributing to the susceptibility response [25]. This upper bound does not necessarily rule out the RKKY coupling proposed in Ref. [11], where it was suggested that the magnetic noise is due to RKKY-mediated spin diffusion. However, spin diffusion mediated by an isotropic interaction as considered in Ref. [11] conserves total angular momentum and thus the total magnetic moment (assuming no g-factor variations). Thus, the observation of a paramagnetic response from isolated rings, which are smaller than the pickup loop [12] and thus couple to our sensor mostly through their total magnetic moment, is inconsistent with this diffusion model. Nevertheless, anisotropic spin-spin interactions, such as dipolar coupling, could in principle determine the relaxation dynamics.

We finally discuss a few anecdotal observations. We observed comparable values of ϕ_1 on two other samples, one similar to sample I, but on a Si substrate with an approximately 1 μm thick wet thermal oxide [15], and one similar to sample II, but with Ag substituted for the top two Au layers. The Ag films showed a substantial spatial variation of the magnetic response. This inhomogeneity could be due to an inhomogeneous surface oxidation or other chemical contamination. We find that the contributions from different layers on sample II are in general not additive, which most likely means that the spin population is concentrated at surfaces or interfaces. The nonlinear response and ϕ_2/ϕ_1 vary significantly between different samples and different layers [Figs. 2(d)–2(g)]. Even though the nonlinearity seen in sample II is predominantly cubic, its magnitude and T dependence are inconsistent with the saturation of the equilibrium response at finite field. The relatively small ratios of the hysteretic and nonlinear components to ϕ_1 indicate that the majority of the spins contributing to the latter relax fast compared to the measurement frequency. The increase of ϕ_2 with frequency is qualitatively consistent with $S_\Phi(\omega)$ varying slower than $1/\omega$, as observed in some SQUIDs [1,14].

In summary, we have measured the susceptibility of micropatterned thin films. Different samples showed similar linear responses corresponding to an area density of unpaired spins on the order of 0.4 spins/nm^2. The spins on our Au films appear to be weakly coupled to conduction electrons. The out-of-phase component of the susceptibility gives direct experimental evidence for the hypothesis that the $1/f$ flux noise seen in SQUIDs and superconducting qubits is due to fluctuating spins [8].

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