Design for a multifrequency high magnetic field superconducting quantum interference device-detected quantitative electron paramagnetic resonance probe: Spin-lattice relaxation of cupric sulfate pentahydrate (\(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\))

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We have designed a spectrometer for the quantitative determination of electron paramagnetic resonance (EPR) at high magnetic fields and frequencies. It uses a superconducting quantum interference device (SQUID) for measuring the magnetic moment as a function of the applied magnetic field and microwave frequency. We used powdered 2,2-diphenyl-1-picrylhydrazyl to demonstrate resolution of g-tensor anisotropy to 1 mT in a magnetic field of 3 T with a sensitivity of \(10^{14}\) spins per 0.1 mT. We demonstrate multifrequency operation at 95 and 141 GHz. By use of an aligned single crystal of cupric sulfate pentahydrate (chalcanthite) \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\), we show that the spectrometer is capable of EPR line shape analysis from 4 to 200 K with a satisfactory fit to a Lorentzian line shape at 100 K. Below 100 K, we observed line-broadening, g shifts, and spectral splittings, all consistent with a known low-dimensional phase transition. Using SQUID magnetometry and a superconducting magnet, we improve by an order of magnitude the sensitivity and magnetic field range of earlier power saturation studies of \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\). We were able to saturate up to 70% of the magnetic moment with power transfer saturation studies at 95 GHz, 3.3 T, and 4 K and obtained the spin-lattice relaxation time, \(T_1 = 1.8\) ms, of \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\) at 3.3 T and 4 K. We found an inverse linear dependence of \(T_1\), in units of seconds (s) at 3.3 T between 4 and 2.3 K, such that \(T_1 = 0.016 \cdot \text{K} \cdot \text{s}^{-1} \cdot 0.0022\) s, where \(\tau\) is the absolute bath temperature.

The quantitative determination of EPR is difficult with standard EPR techniques, especially at high frequencies or fields. Therefore this technique is of considerable value. [DOI: 10.1063/1.1808893]

I. INTRODUCTION

High-frequency electron paramagnetic resonance (HF–EPR) is proving itself to be a powerful technique for the characterization of magnetic materials.\textsuperscript{1–6} It can be used for accurate and sensitive measurements of spin Hamiltonian parameters such as the hyperfine field (\(A\)), Lande g tensor (\(g\)), which tend to scale as the applied magnetic field (\(H\)), spin exchange energy (\(J\)), spin–spin interactions due to the crystalline field (\(D\)), chemical and magnetic structure, electron spin density, spintronic material properties, and evaluation of radiation dosage or dosimetry.\textsuperscript{7} There are currently many laboratories that specialize in development of HF–EPR systems,\textsuperscript{1–6} and a commercial spectrometer is available operating at 95 GHz. These instruments generally characterize EPR by means of phase-lock detection of radio frequency (rf) fields using Schottky diodes and bolometry, which have inherent problems for quantitative analysis. Here, we describe instrumentation in which EPR is characterized by means of the quantitative observation of the change in magnetic moment due to microwave stimulation using a sensitive magnetometer based on a superconducting quantum interference device (SQUID).

In general, HF–EPR is performed using one of two configurations. In the first,\textsuperscript{3,6} the sample is contained within a resonant cavity and the change in quality factor (\(Q\)) is measured, from which the imaginary component, \(\chi''\), of the microwave susceptibility is determined, or the change in resonant frequency of the cavity is measured from which the real component \(\chi'\) is derived. The second configuration is a single-pass or transmission measurement where the sample is mounted inside a waveguide and the change in transmitted radiation power is measured as a function of the swept magnetic field.\textsuperscript{2,5} The former has the advantage of high sensitivity and discrete observation of \(\chi'\) and \(\chi''\), whereas the latter has the advantage of ease of use, especially for multifrequency measurements. Here we describe a transmission-type approach.

The method uses standard SQUID magnetometry to measure the magnetic moment, expressed as the molar susceptibility \(\chi\) (in units of m\(^3\)/mol),\textsuperscript{8} which, for a paramagnetic material is given by

\[
\chi = \frac{M}{H} = \frac{C}{T - \theta}.
\]

where \(M\) is the molar magnetization in A m\(^2\)/mol, \(H\) is the applied dc magnetic field in A/m, \(C\) is the Curie constant in m\(^3\) K/mol, \(T\) is the bath temperature, and \(\theta\) the Curie–Weiss temperature, both in units of kelvins.

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When a paramagnetic sample is illuminated with a continuous-wave rf field the magnetization $M$ decreases near the EPR. The steady-state solution for $M$ is given by the Bloch equation\(^9\)

$$M_Z = M_0 \frac{1 + (\omega_B - \omega)^2 T_2^2}{1 + (\omega_B - \omega)^2 T_2^2 + (\gamma_e \mu_0 H_1)^2 T_1 T_2},$$

(2)

where $\mu_0 = 4\pi \times 10^{-7}$ H/m is the permeability of free space, $H_1$ is the magnetic component of the microwave excitation field of angular frequency $\omega$, in A/m, $\gamma_e$ is the gyromagnetic ratio for the electron, in rad s\(^{-1}\) T\(^{-1}\), $\omega_B$ is the Larmor frequency (angular frequency corresponding to field $H$), $M_0$ is the equilibrium magnetization in the presence of a field $H$, and $T_1$ and $T_2$ are, respectively, the longitudinal and transverse relaxation times. Inspection of Eq. (2) indicates that upon application of the $H_1$ field at resonance, $M_Z$ is reduced by $[1 + (\gamma_e \mu_0 H_1)^2 T_1 T_2]^{-1}$. Previous experiments\(^{10}\) that used a vibrating sample magnetometer and a microwave cavity at 14.5 GHz reduced $\chi$ by 96% and obtained a value for $T_1$ of $\sim 40$ ms. Here, we build upon this work and use SQUID magnetometry and a superconducting magnet to increase the sensitivity by at least an order of magnitude, a sample the size of 6 mg instead of 100 mg, and an applied magnetic field of 5 T instead of 0.5 T, and examine the field dependence of the spin-lattice relaxation time. There have been experiments using a SQUID to examine the enhanced magnetic relaxation of molecular nanomagnets in a resonant cavity;\(^{11}\) other work;\(^{12}\) uses a complex setup of micro-Hall bars and a dilution refrigerator at millikelvin temperatures to examine the photon-assisted tunneling of the nanomagnet Fe\(_8\); and very recently, field swept EPR using microsquids at low temperatures <1 K on the $S=1/2$ molecular system Fe\(_{15}\) as well as a preliminary report on Fe\(_8\) at temperatures <1 K.\(^{13,14}\) The design outlined here uses widely available commercial products to obtain field swept quantum EPR spectra over a large range of temperatures (1.8–200 K), magnetic fields (0–5 T), frequencies (up to 141 GHz) and explicitly obtains $T_1$ lifetimes of $S=1/2$ systems as a function of the absorbed microwave power. Since $\chi$ is generally considered to be a bulk parameter, whereas traditional EPR is a local probe, this technique may be complementary to both traditional EPR and susceptibility studies.

II. EXPERIMENT

We used a commercial SQUID magnetometer capable of field sweeps from 0 to 7 T and temperature sweeps of 1.8–400 K. This initial probe design was manufactured with a view to ease of integration into the existing commercial magnetometer. Figure 1 shows the experimental setup. The hollow stainless steel tubing used for sample mounting for susceptibility studies was, in fact, appropriately sized for the 75–110 GHz $W$ band, and calculations determined that the fundamental TE\(_{11}\) mode propagates from $\sim 64$ to 110 GHz. However, stainless steel is very lossy, so we replaced it with thin-wall round brass tubing, labeled “round waveguide” of the same approximate dimensions (3.175 mm outer diameter by 2.54 mm inner diameter) and 125 cm in length to integrate into the existing system of stepper motor, airlock assembly, cryostat, magnet, and SQUID pickup loops, as labeled. Brass tubing represents a compromise between good microwave transmission and thermal insulation. A homemade transition from coin-silver rectangular $V$-band WR-15 waveguide to the circular brass waveguide was formed by drilling a 0.125 diameter hole into one end of a 2 in. piece of $V$-band (50–75 GHz) waveguide with UG-385/U flanges on both ends, and then soldering the brass tube into the drilled hole. This then allows conventional microwave assembly to be mated to the undrilled flanged end. In general, oversized waveguide (hence, the $V$ band, as opposed to $W$-band fittings) was used for HF–EPR studies to minimize microwave attenuation and allow for a wide frequency range. As shown in Fig. 1, the probe is connected to, by use of flanges, a high $f$-band $3400$ mW (as measured by bolometry) 95 GHz or a 141 GHz commercial klystron) through a 95 GHz isolator to prevent reflections into the klystron, a $W$-band attenuator for saturation studies, and a directional coupler (in this case $V$ band to minimize loss). A detector/mixer at the coupled port monitors the frequency and reflected/incident power. The other end of the three-port directional coupler was connected to the waveguide transition.

The whole probe assembly is mechanically oscillated parallel to the waveguide axis by a stepper motor through the SQUID loops in order to obtain the magnetic moment. The SQUID magnetometer technique is detailed in Ref. 15. Note that this probe design would be effective for basic Faraday extraction of the magnetic moment as well for vibrating-sample magnetometry,\(^{10}\) which may allow for access to higher magnetic fields.

The background magnetic moment of the probe is 2 X $10^{-6}$ A m\(^2\) at 4 K, which is a factor of 30 below that of CuSO\(_4\)·5H\(_2\)O. The SQUID magnetometer pickup loops form a second-order gradiometer, and therefore the sample holder, with the sample in the middle, should be homogenous throughout the oscillation length. In order to approximate a uniform background from the waveguide sample holder, we attached an extension tail (labeled balancing waveguide in Fig. 1) to the end of the waveguide.

Figure 1 shows that our measurements utilize the Fara-
day geometry in which the microwave propagation is parallel to the static magnetic field. We currently estimate by means of variable attenuators and a network analyzer that this probe has about 6 dB of attenuation from the source to the sample, which results in 100 mW of power incident on the sample at 95 GHz, at room temperature. The temperature dependence of the attenuation is under investigation. The sample mass for these experiments was 6 mg. The sample filled the entire diameter of the waveguide and was approximately 3 mm in length. The sample oscillation amplitude was 4 cm to minimize line broadening due to magnetic field inhomogeneity. Each value of the magnetic moment was averaged four times to improve the resolution at these higher fields. 4,16 In Fig. 2, the triangle data points with no applied microwaves show the expected constant value of $\chi$ as a function of magnetic field. Upon microwave irradiation at 95.510 GHz, a minimum and a small shoulder in $\chi$ are observed. We attribute this structure to $g$-tensor anisotropy at 95 GHz and 50 K. We assign the main peak labeled $g \perp$ to those crystallites whose magnetic axis is perpendicular to the applied field, and assign a minor peak, labeled $g ||$, to those crystallites whose magnetic axis is aligned parallel to the applied Zeeman field. Here, we take $2/3 g \perp + 1/3 g ||$ as a field marker to correspond to the X-band isotropic value of $g_{iso} = 2.0036$. We then obtain $g \perp = 2.0039$ and $g || = 2.0028$, which is in good agreement with early anisotropic observations 4 at 250 GHz. For a discussion on the behavior of DPPH at high fields please see Ref. 16. The halfwidth (as indicated by the arrows) of the $g \perp$ transition is 0.9 mT. The signal-to-noise ratio (S/N) defined here as the maximum signal divided by the standard deviation of the baseline, is 12.300. If we define the minimum number of detectable spins as that which gives a S/N of 3:1, then for these conditions, a powder spectrum of lines of 1 mT at 50 K with four scans per point would be $10^{15}$ spins per 0.1 mT. These data show that 0.0009 T resolution in a 3.300 T field can be obtained for concentrated spin systems by using this technique. Further experiments utilizing known narrow lines of single aligned crystals at high frequencies would be necessary to determine the absolute resolution and sensitivity at these fields and temperatures.

We investigated whether this technique can yield a corresponding increase in the resolution of the $g$ tensor as described by Eq. (3) at the highest fields. The inset to Fig. 2 shows the EPR spectrum at 141 GHz and 5 T, and we observe a line broadening ($\Delta H_{1/2} = 1.8$ mT). Hence, the principal components of the $g$ tensor are not readily differentiated. We mainly attribute this line broadening to field inhomogeneity across the sample path. However, at the least, we have established, a resolution of 0.0018 T in an applied field of 5 T, which is consistent with the specified magnet homogeneity of $10^{-4}$ parts in 1 cm diameter spherical volume. Single-crystal measurements and smaller scan lengths may improve the resolution at these higher fields.

The spin Hamiltonian for DPPH can be represented by

$$H = \mu_B g \cdot \mu_B H \cdot S + I \cdot A \cdot S,$$

where $\mu_B$ is the Bohr magneton, $g$ is the Landé $g$ tensor, $H$ is the applied Zeeman field, $S$ and $I$ are, respectively, the electronic and nuclear spin operators, and $A$ is the hyperfine interaction tensor. In the solid state as a concentrated system, the second term has been shown to be averaged out by spin exchange, so that we are only interested in the field-dependent Zeeman interaction, resulting in the well known resonance condition $\hbar \nu = g \mu_B \mu_B H$, where $\hbar$ is Planck’s constant and $\nu$ is the microwave frequency. At low frequencies $<20$ GHz, a powder sample of DPPH exhibits a single exchange-narrowed line whose width is of the order of 0.1–0.2 mT; for some samples $g$-tensor anisotropy will result in line structure at higher frequencies. 4,16 In Fig. 2, the triangle data points with no applied microwaves show the expected constant value of $\chi$ as a function of magnetic field.
B. Single-crystal SQUID–EPR of copper sulfate as a function of temperature

In this section we demonstrate that SQUID–EPR is useful as a general HF–EPR tool by characterizing the temperature dependence of the 3d,9 S=1/2, CuSO₄·5H₂O system. The crystal structure indicate that there are two equivalent Cu⁺⁺ ions in the triclinic unit cell. The geometry of each is nearly octahedral, the structure consisting of four water molecules in a plane and two oxygen atoms; the angle between the planes of water molecules of the two ions is 82°. The Cu⁺⁺ ions form two independent magnetic systems with an exchange interaction of ~10 GHz. This results in a single exchange-narrowed line at the X band (~9 GHz), which interaction is dominant at higher temperatures. The third term is the Raman mechanism. The second term is the Orbach process where a two-phonon process occurs, as a function of decreasing temperature. The orientation of broadening and resonance shifts is consistent with the presence of internal demagnetizing fields or short-range order effects preceding a phase transition. These data indicate that this technique is capable of EPR line shape and line-shift analysis as a function of temperature up to at least 200 K.

C. Power transfer studies of $T_1$ at 3.3 T and 95 GHz

We also built on previous work done by Candela et al. to further characterize the CuSO₄·5H₂O system and demonstrate the determination of $T_1$ by saturation methods using SQUID–EPR at high magnetic fields. The temperature and field dependence of the spin lattice relaxation $T_1$ are composed of three general mechanisms such that

$$T_1^{-1} = \Delta H T + B T^2 + C \exp(-\Delta/kT).$$

The first term is the direct process, where the energy emission is through one phonon and $x$ is generally equal to 2 for a non-Kramer’s ion (integer spin), or 4 for a Kramer’s ion (half-integer spin). The second term is the Raman mechanism, a two-phonon process via an intermediate magnetic ion virtual state, and $y$ can take values of 5, 7, or 9; therefore, this mechanism is dominant at higher temperatures. The third term is the Orbach process where a two-phonon process occurs via a real state with an excitation energy $\Delta$. At low (liquid helium) temperatures the direct process is dominant, and here we adopt the formalism of Candela et al. and Bolger with the assumption that the relaxation process can be described by a single longitudinal relaxation time that is much slower than the transverse relaxation time, $T_2$, as well as all other processes such as spin exchange, spin diffusion, and lattice-bath heat transfer. Based on these assumptions it has...
FIG. 5. The degree of saturation \((1-R)\) of CuSO\(_4\)-SH\(_2\)O as a function of the applied microwave \((\nu=95.301\text{ GHz})\) power per mol. The circles (○) are the experimental data, and the drawn line (main figure) is a fit to Eq. (5) that indicates \(T_1 = 1.8\text{ ms}\) at 3.3 T. The inset shows \(T_1\) as a function of inverse temperature over the range 6–2 K. We found an inverse linear dependence of \(T_1\) between 4 and 2.2 K, as expected for a direct process. The drawn line is a fit to Eq. (4).

been shown that \(T_1\), in units of seconds (s), is\(^{10,27}\)

\[
T_1 = \frac{\chi_0 \mu_0 H^2}{P_a} (1 - R),
\]

where \(\chi_0\) is the direct current susceptibility (in units of m\(^3\)/mol) in the absence of microwave irradiation, and \(R\) is the ratio \(\chi'/\chi_0\) with \(\chi_0\) being the magnetic susceptibility when the sample absorbs microwave irradiation of power \(P_a\) (in units of W/mol) at the resonance peak, and \(H\) is the applied magnetic field in the \(z\) direction, in units of A/m. Figure 5 shows the dependence of the magnitude of \((1-R)\) as a function of the power absorbed \((P_a)\) by the sample for 95 GHz irradiation and 3.3 T applied field. From a fit of the linear region we obtained, \(T_1 = 1.8\text{ ms}\). Here, with the assumption that the change in reflected power (40\%) at resonance relative to off-resonance is indicative of the lower limit of power absorbed, and that the upper limit is the possible power deliverable of 200 mW at 4 K, we use \(P_a = 100\text{ mW}\), and believe this number is accurate to within a factor of 2–4. The previously determined value\(^{10}\) of \(T_1\) at 0.5 T and 4 K was 40 ms; therefore these results preliminarily indicate that the field dependence of the lifetime varies as \(H^{-2}\), and not as \(H^{-4}\), which is a surprising result since Cu\(^{2+}\) is a Kramer’s ion, however more data points are needed. Due to the yield of quantitative knowledge of the degree of saturation \(at\ any\ level\), this technique allows for the evaluation of \(T_1\) in the low-power (linear) saturation regime [see Eq. (5)], whereas conventional EPR studies generally require approaching or exceeding the high-power nonlinear regime. This is important at high frequencies where the available microwave power is usually limited.

Next, we examine the temperature dependence of \(T_1\) at constant power and field. The saturation level was set around 14\% at 2 K. This level of saturation is in the linear region of \(1-R\) vs \(P_a\), and this power level minimizes possible crystal heating. The inset to Fig 5 provides the lifetimes as a function of inverse temperature, and, in agreement with earlier work,\(^{10}\) a linear fit is obtained in the region of 4–2.3 K with a dependence on \(T_1\) of \(T_1 = 0.016\text{ K} \cdot \text{s}^{-1} \cdot \tau^{-2} \cdot 0.0022\text{ s}\), where \(\tau\) is the bath temperature in kelvin, indicating a dominance of the direct relaxation process outlined in Eq. (4). We also investigated \((1-R)\) as a function of temperature at 141 GHz and 5.5 T, and found that \(T_1\) was linear between 2.5 and 4 K and saturation levels of up to 40\% were obtainable. These results indicate that this technique is capable of determining the temperature and field dependences of the spin-lattice relaxation time of \(S=1/2\) systems at high magnetic fields and microwave frequencies.

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\(^{13}\)W. Wernsdorfer, A. Muller, D. Mailly, and B. Barbara, e-print cond-mat/ 0404410 (2004); Europhys. J. (to be published).

\(^{14}\)M. Bal et al., e-print cond-mat/0404448 (2004).


\(^{27}\)B. Bolger, Physica (Amsterdam) 26, 761 (1960), and references therein.