Thermomagnetic properties of the Finland trityl radical

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The Finland trityl paramagnet is characterized by magnetic susceptibility and a new form of quantitative electron paramagnetic resonance (EPR) that utilizes a superconducting quantum interference device (SQUID) as a detection method. This radical is of interest due to its use as a dynamic nuclear polarization agent as well as a potential magnetic refrigerant and quantum computing bit. The SQUID-EPR data show that the EPR linewidth of a concentrated trityl powder decreases dramatically from 4.4 to 1.4 mT as the temperature is increased from 1.8 to 10 K. The quantitative nature of SQUID-EPR is used to thermodynamically quantify the EPR energy transfer times and saturated fractions. At 95 GHz and 1.8 K, only 40% of the spins are in resonance at the onset of saturation. Conventional dc magnetic susceptibility over 1.8–150 K indicates an $S=1/2$ Curie–Weiss relationship with little long range interaction. Magnetization versus applied field at 1.8 and 4 K fits a Brillouin function with $>80\%$ electronic polarization at a normalized field of $g\mu_B\mu_0 H/kT \approx 3$. These results provide information required for theoretical modeling and engineering of the trityl radical for a wide range of applications. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073992]

I. INTRODUCTION

Paramagnets generate a new wave of interest due to a manifold of advanced applications in medicine, cryotechnology, and electronics. These applications include dynamic nuclear polarization (DNP) for enhancement of nuclear magnetic resonance and magnetic resonance imaging (MRI),^{1–5} magnetic cooling,^{6,7} electron paramagnetic resonance imaging (EPRI),^{8,9} and quantum computing.^{10,11} Paramagnetic systems include transition metal ions and organic radicals. Unfortunately, broad EPR linewidths and materials toxicity rule out many of these paramagnets for most of the applications. There exists an interesting class of carbon-centered persistent radicals known as trityls. The trityls possess very narrow linewidths in both the solid and solution phases. Many variants are low in toxicity and thus useful for medical applications. We briefly discuss the relevance to this work of each application.

DNP is an exciting new approach to MRI that transfers the polarization of an electron-based paramagnet to the magnetic nuclei of a compound of interest. DNP has the potential to increase carbon based MRI sensitivity by many orders of magnitude, allowing direct visualization of a medicinal agent's flow and biointeractions through the body. The trityls form glassy solid solutions at low temperatures with organic compounds. These glasses are irradiated near the trityl electron paramagnetic resonance (EPR) frequency, generally from 95 to 140 GHz, and at low temperatures <2 K where the electron spins are close to being fully polarized.^{1,2,5} Polarization is transferred from the paramagnetic trityl to the target nuclei of compounds of medicinal interest such as

metabolites.^{1,2,5} The trityl can be removed during solution transfer to room temperature by an ion exchange column.^{1,2} The metabolite is then quickly injected into a biological receptor, such as a mouse, and subsequently imaged spectroscopically, to observe comparative chemical changes within normal and tumor cells.⁵ Electronic polarization, spin relaxation, linewidths, and linewidth homogeneity are among factors of the DNP theory of MRI enhancement.^{3,12} Thus, a quantitative evaluation of the physics of the magnetization and EPR of the trityl radical at low temperatures and high frequencies are of both practical and theoretical interest.

The trityls find use as EPRI quantitative oxygen concentration reporter agents.^{8,9} The mechanism is based on the broadening of the trityl EPR line in solution due to collisions with oxygen (diradical) molecules. This line broadening can be correlated with oxygen concentration.^{8,9} The promise of EPRI oximetry is noninvasive *in vivo* tumor maps of the oxygen concentration. The linewidths are also a function of the trityl concentration due to intermolecular Heisenberg spin exchange and dipole-dipole interactions. While correlations of low temperature solid state and room temperature solution phase phenomena are difficult, a determination of the temperature dependence of the magnetic susceptibility, spin exchange, and dipolar energies of the pure trityl system will be useful in understanding and modeling the behavior at room temperature.

Magnetic cooling holds the promise of an inexpensive and efficient method to obtain temperatures in the millikelvin to 20 K range.^{6,7} Magnetic cooling is important due to limited helium supplies as well as in space applications with low gravitational fields.¹³ A trade-off exists between the lowest attainable temperature and the refrigeration power.⁷ A high spin concentration will have a high refrigeration power, but

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FIG. 1. The inverse χ_p as a function of temperature. The solid line is a fit to Eq. (1) and the Curie–Weiss temperature is ~ -0.7 K (consistent with very small intermolecular interactions). The structure of the trityl radical is provided in the inset (the R -groups are equivalent to the drawn substituent).

the presence of spin-spin exchange and dipolar interactions will limit the lowest temperature. An earlier report proposed a new class of tunable refrigerants based on the variable spin concentrations of a series of Cr(V) tetraperoxides.⁷ The ease with which the trityl spin concentration is controlled via glassy mixtures may render them as viable, tunable, adiabatic demagnetization materials. However, an understanding of the magnetization and internal fields is necessary for such conclusions.

Quantum computing is touted as possessing tremendous advantages over present day computing techniques, especially in the realm of information coding. EPR spin systems possess inherent advantages over nuclear spin systems. The ratio of electronic to nuclear thermal polarization is orders of magnitude larger, and generally, sensitivity scales with increasing observation frequencies. A wide range of materials are of interest in the literature for EPR based quantum computing. Some recent novel compounds include the endohedral fullerenes N@C₆₀ and P@C₆₀ (this notation refers to a nitrogen or phosphorus atom trapped within a C₆₀ molecule),¹¹ the single molecule magnets,¹⁴ and transition metals such as Cr(V).¹⁵ The attractive features of these materials are narrow linewidths in the solid and liquid states and long spin lifetimes. Knowledge of the solid state spin parameters at low temperatures would be of use to gauge the efficacy of the trityls for such applications.

A new high-frequency EPR technique has been developed that uses a superconducting quantum interference device (SQUID) to detect the change in the dc magnetic moment due to resonant rf irradiation.^{16–19} This technique can quantify the spin moment of nanomagnetic materials as a function of microwave irradiation (50–141 GHz), magnetic field (0–7 T), and temperature (1.8–400 K). Here, we apply the SQUID-EPR technique to characterize tris(8-carboxy-2,2,6,6-tetramethylbenzo[1,2-d:4,5-d']-bis(1,3-dithiol-4-yl)methyl sodium salt (“Finland trityl”). The structure of this radical is shown in the inset of Fig. 1. The SQUID-EPR measurements are correlated with conventional magnetic characterization techniques such as temperature dependence of the magnetic susceptibility and magnetic field dependence

of the magnetization. The results are discussed in terms of their relevance to the previously discussed applications.

II. EXPERIMENTAL

The SQUID-EPR work was done by using a 95 GHz microwave klystron at the NIST in conjunction with a commercial SQUID magnetometer, details of which are provided in Refs. 16–18. This commercial magnetometer was also used for conventional magnetization as a function field and temperature. The trityl sample was provided by the Center for EPR Imaging *In Vivo* Physiology in Chicago, IL.²⁰ The measurement took place after 3 years in a freezer at -20 °C, and subsequent transport of 2 days at room temperature and ambient humidity. The measured sample was composed of green flakes that were lightly crushed. Conventional single-pass EPR absorption measurements were made using a home built 95 GHz EPR at IIT in Chicago, IL. This consisted of a 95 GHz single frequency Gunn diode source, oversized copper tubing waveguide, and a commercial 0–9 T, 1.8–400 K magnetic measurements platform.²¹ However, all data for the single-pass EPR were collected in the nonderivative (no phase-lock detection) or direct absorption mode.

III. RESULTS AND DISCUSSION

The magnetic susceptibility χ (in units of m³/mol) is the sum of the diamagnetic contribution χ_d and paramagnetic contribution χ_p such that

$$\chi \equiv \frac{M_Z}{H_Z} = \frac{C}{T - \theta} + \chi_d, \quad (1)$$

where M_Z is the longitudinal molar magnetization (in units of A m²/mol), H_Z is the applied magnetic field that defines the z -axis, C is the Curie constant (in units of m³ K/mol), T is the bath temperature, and θ is the Curie–Weiss temperature. We use an empirical method outlined previously to obtain the parameters by plotting the inverse total susceptibility plus a constant versus temperature until the best fit is found for a linear dependence on T in the 2–80 K region.²² We obtain $\chi_d = -4.8 \times 10^{-9}$ m³/mol (-3.8×10^{-4} emu/mol). This value is then subtracted out which gives the paramagnetic susceptibility χ_p . Figure 1 shows χ_p^{-1} from which the inverse slope provides $C = (3.6 \pm 0.2) \times 10^{-6}$ m³ K/mol (0.29 emu K/mol) and the x -intercept provides $\theta = -0.7 \pm 0.2$ K; the negative value of θ indicates antiferromagnetic interactions. The ratio of available spins to total possible spins, or $C_{\text{obs}}/C_{\text{theor}}$ is 0.77 [where C_{theor} for $S=1/2$ and $g=2$ is 4.71×10^{-6} m³ K/mol (0.375 emu K/mol)]. This discrepancy is attributed to sample deterioration and hydration. While trityls can be prepared in 90% or greater purity and are highly stable when frozen, they are known to deteriorate at room temperature as well as being light sensitive.

In Fig. 2 the magnetization as a function of swept field from 0 to 7 T is given at both 4 and 1.8 K. These data show that at these temperatures the trityl behaves as a simple paramagnet. The inset shows the moment in Bohr magnetons per molecule versus the dimensionless parameter η where $\eta = g\mu_B\mu_0 H_z/kT$ (g is the electronic g -factor and $\mu_0 = 4\pi$

FIG. 2. dc Magnetization M_z as a function of field at 1.8 and 4 K of the trityl powder. Going from 4 to 1.8 K dramatically increases the polarization at 3.4 Tesla. At 7 T there is much less polarization gain upon varying the temperature from 4 to 1.8 K. The inset shows the magnetization in Bohr magnetons per molecule as a function of the reduced magnetization for both 4 and 1.8 K. These data fit a Brillouin function (drawn) line consistent with a spin-half system.

$\times 10^{-7}$ H/m is the permeability of free space). For an $S = 1/2$ system the magnetization should saturate at $1 \mu_B/\text{molecule}$. The drawn line is a fit to an adjusted Brillouin ($B_{J(\eta)}$) function, $AB_{J(\eta)}$, for $J=S=1/2$, where $L=0$, and L and J are the orbital and total angular momenta, respectively, such that $M=0.76J^{-1}[(J+1/2)\coth(J+1/2)\eta - 0.5(\coth(\eta/2))]$. The leading term of 0.76 is a normalization factor consistent with the data in Fig. 1 and is also attributed to sample degradation and hydration. These data indicate that the bulk magnetic properties of the trityl are well behaved up to 7 T and conducive to the outlined applications.

When a paramagnetic sample is illuminated with a continuous-wave radio-frequency (rf) field, the magnetization M_z decreases near the EPR frequency. The steady-state solution for M_z is given by the Bloch equation solution,²³

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

where H_1 is the magnetic component of the microwave excitation field of angular frequency ω , $\gamma = g\hbar e/2m_e$ is the gyromagnetic ratio for the radical, $\omega_B = \gamma \mu_0 H_z$ is the Larmor frequency, M_0 is the equilibrium magnetization in the presence of a field H_z , and T_1 and T_2 are the longitudinal relaxation (energy transfer) and transverse (spin-spin) relaxation times, respectively. Inspection of Eq. (2) indicates that upon application of the H_1 field at resonance, M_z is reduced by a factor of $[1 + (\gamma \mu_0 H_1)^2 T_1 T_2]^{-1}$.

This effect is demonstrated in the SQUID-EPR of a powder sample of the trityl radical at a cooling bath temperature T_b of 5 K in Fig. 3. The exact sample temperature is not known but is expected to be higher in the presence of microwaves. At 96 GHz irradiation there is an asymmetric dip in M_z (solid line). We attribute the asymmetry to g -tensor an-

FIG. 3. Longitudinal magnetization as a function of magnetic field under microwave irradiation of the trityl radical showing SQUID-detected EPR. Inset: smoothed first derivative (in arbitrary units) from which $g_{\perp}$ is assigned to the baseline crossing and $g_{\parallel}$ is assigned to the maximum as indicated. $\Delta H_{p.p.} = 1.0$ mT is the peak-to-peak linewidth attributed to the $g_{\perp}$ transition as indicated by the arrows.

isotropy, as has been observed in other works using dilute solid solutions.^{24–26} The inset line is a smoothed first derivative and, in accordance with standard EPR practice, we assign the zero crossing to $g_{\perp}$ and the maximum to $g_{\parallel}$. Smoothing is required before taking the first derivative due to noise. We attribute the noise to partially aligned microcrystallites at low temperatures and high fields due to the absence of sample grinding. No further anisotropy was resolved at this temperature with the pure sample. The relative g -anisotropy $\Delta g/g_{\text{iso}}$, where $\Delta g = g_{\perp} - g_{\parallel}$ and $g_{\text{iso}} = ((2/3)g_{\perp} + (1/3)g_{\parallel})$ was found to be $(3.0 \pm 0.2) \times 10^{-4}$ for our powder (crushed flakes) sample, compared to 3.37×10^{-4} for the glassy water-glycerol solution (0.2 mM) in Ref. 24 at 100 K, and 3.16×10^{-4} in Ref. 25 for a dilute solution (15 mM) in propenediol at 1 K and 70 GHz. This agreement is reasonable given the different conditions such as temperature and radical concentration. The width at half-height $\Delta H_{1/2}$ of the full spectrum at 5 K was 2.3 mT, as indicated. In terms of a conventional EPR derivative presentation, the peak-to-peak linewidth of the $g_{\perp}$ transition is 1.0 ± 0.1 mT, compared to 0.8 mT of Ref. 24. This represents good agreement between SQUID-EPR technique and conventional EPR, especially since broadening of the concentrated system with temperature is present (see below). The 1.0 ± 0.1 mT linewidth is the narrowest observed to date by our SQUID detected EPR techniques.

In Fig. 4 the dc magnetization of the Finland trityl as a function of magnetic field at a bath temperature of 1.8 K and microwave irradiation of 296 GHz is shown. This EPR transition has a linewidth of 4.4 mT. The inset shows the linewidth as a function of temperature; there is significant narrowing in the SQUID-EPR data of 4.4–1.4 mT as the bath temperature increases to 10 K. We also did conventional single-pass absorption EPR, as shown by the squares. A clear

FIG. 4. High-frequency SQUID-EPR spectra of trityl radical powder at a bath temperature of 1.8 K and 96 GHz. There is considerable broadening compared to Fig. 3. The inset shows the full powder spectrum width at half-height as a function of bath temperature for both SQUID-detected (triangles) and conventional detection (squares). Lines are a guide for the eyes.

increase in linewidth was observed as well. However, mixtures of dispersion and absorption complicate linewidth measurements, and the use of different cryostats complicates relative temperature comparisons. At temperatures from 20 to 100 K, we found the linewidth to be constant at 1.0 ± 0.3 mT.

The exact nature of the broadening is not clear; however, temperature dependent broadening can be a function of internal demagnetization fields, or short range order approaching a phase transition.^{16,22,27} These results are in contrast to recent EPR work on diluted trityl systems which exhibited little to no linewidth dependence on temperature down to 1 K.^{25,26} This indicates that at low temperatures, the EPR linewidth is highly dependent on the trityl concentration, whereas at temperatures above about 10 K, there is little dependence. It would be of interest to examine the linewidth as a function of concentration, as well the orientation-dependent single crystal linewidth. These data show that the linewidth of the trityl system can be manipulated by concentration over a fourfold range at 1.8 K.

For a linearly polarized electromagnetic rf field and a system in thermal equilibrium, the power absorbed P_a (in W/mol) in a transition between the lower and the upper states is $P_a = (1/2)\omega\chi''\mu_0 H_1^2$, where ω is the angular frequency, χ'' is the imaginary component of the transverse susceptibility in m^3/mol , and H_1 is the magnitude of the magnetic component of the oscillating field, which is proportional to the square root of the microwave power. Given that the work done per mole on a system of magnetic energy U_m at constant field H_z changes U_m such that

$$\delta U_m = \mu_0 H_z \delta M_z, \quad (3)$$

and the phenomenological Bloch equation for the time dependence of M_z is

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}, \quad (4)$$

then the time derivative of Eq. (3) gives

FIG. 5. Change in magnetic energy as a function of the absorbed resonant microwave power at 96 GHz at $g_{\perp}$. The right-hand axis shows the percent suppression of the magnetization.

$$\frac{dU_m}{dt} = P_a = \frac{(M_0 - M_z)\mu_0 H_z}{T_1}, \quad (5)$$

where M_0 is the magnetization in the absence of microwave irradiation and M_z is the steady-state magnetism in the presence of microwave irradiation. In terms of susceptibility, $P_a = \chi_0 \mu_0 H_z^2 (1 - \chi_{\text{on}}/\chi_0) T_1^{-1}$, where χ_0 is the molar dc susceptibility.^{16,28} Hence, for an $S=1/2$ system, by measuring the magnetic susceptibility and χ_{on} is the susceptibility in the presence of microwaves in the presence and absence of microwave irradiation and a knowledge of P_a , one can explicitly determine the energy transfer time under continuous-wave irradiation.^{16,28}

At low temperatures the energy transfer and hence the sample and spin temperature are complicated by the possible presence of a phonon blockade, which limits the flow of heat from the phonons to the cryostat, as well as nonresonant microwave heating. In the context of this paper T_1 refers to the time constant of the heat flow of the combined system of electron spins and phonons to the cryostat. We note that the effect of excess heating would be to decrease the magnetic susceptibility and increase the observed suppression. Discussions of these issues are found in Refs. 17 and 19.

In Fig. 5 we show the change in magnetic energy as a function of the absorbed resonant microwave power at 96 GHz and a bath temperature T_b of 1.8 K. There is a linear region at low powers and a saturated region at higher powers. The beginning of saturation occurs at 40% suppression. In contrast, in single crystals of copper sulfate,^{16,28} and the molecular magnet Fe_8 ,^{17,18} over 80% of the magnetization was suppressed. The very low suppression at saturation for the trityl is attributed to the g -anisotropy present in a powder spectrum. At a field of 3.4250 T only the crystallites whose magnetic easy axes are perpendicular to the Zeeman field are excited and their moment suppressed, while the crystallites whose magnetic easy axes (z -axis) are parallel are unaffected. Saturation of the $g_{\perp}$ components will thus begin between 33% and 66% of the total magnetization depending on the overlap of the g_x and g_y linewidths. These data indicate

that at high trityl concentrations and low temperatures the line is inhomogeneously broadened and hole burning occurs. This is in contrast to Ref. 30 which showed by using spin echo techniques that for dilute systems at 10 K and 140 GHz the line is effectively homogeneous.

The low power linear region in Fig. 5 is fit in accordance with Eq. (5), and T_1 is found to be about 1–2 ms for $g_{\perp}$, with an estimated error of a factor of 2–4, mostly due to uncertainty in the power absorbed estimate.¹⁶ This value is significantly lower than the reported value of 40 ms at 140 GHz and 10 K for a trityl in a frozen water/glycerol glass using saturation recovery spin echo.³⁰

The temperature and field dependences of T_1 are functions of three general mechanisms such that²⁹

$$T_1^{-1} = AH^xT + BT^y + C \exp(-\Delta/kT). \quad (6)$$

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 excitation energy Δ . At 1.8 K the first term in Eq. (6) would be expected to dominate. Since we are at a much lower temperature (1.8 versus 12 K) and magnetic field (3.4 versus 5.1 T), T_1 for our system would be expected to be of the order of seconds, much greater than 40 ms given in Ref. 30 for a dilute system. The exact nature of the concentration dependence of T_1 is not known at this time. Since the linewidth increases with concentration, increased opportunities for spectral diffusion (processes which transfer spin polarization from one position of the spectrum to another) may be a factor, as well as spin-spin interactions due to decreased distance between paramagnetic centers. Further experiments involving the dependence of T_1 and linewidth on temperature and concentration, as well double resonance techniques are planned to answer these questions.

IV. CONCLUSION

We have presented the first study correlating global properties, as measured by dc magnetic susceptibility, with local properties, as measured by EPR, of a member of the trityl family of persistent carbon-centered radicals. We used a neat powder of the Finland trityl as the model compound. The magnetic susceptibility fit the Curie–Weiss law and a Brillouin function for an $S=1/2$ system adjusted for sample deterioration. These data can be used to estimate the electronic polarization over a wide range at low temperatures. This is of importance for applications such as DNP, magnetic cooling, and quantum computing.

The SQUID-EPR data indicated a significant line broadening of the concentrated system at low temperatures. Recent works have indicated that line broadening reduces DNP efficiency.^{25,26} Therefore this result provides a mechanism for the decrease in DNP at high trityl concentrations.

The saturation data indicated that only a limited amount of spins are excited with a narrow band microwave source. We attribute this to g -anisotropy and inhomogeneous broadening due to the buildup of internal fields at low temperatures. This is consistent with the magnetization data that showed the Curie–Weiss temperature of -0.7 K. In terms of magnetic cooling, this magnitude of internal field theoretically indicates that the concentrated trityl system would be of use in the temperature range of ~ 1 –10 K.⁷ Diluted samples would be expected to provide convenient systems that balance cooling loads with desired temperature below 1 K.⁷

T_1 is much shorter for this concentrated system than for dilute systems, which is attributed to spectral diffusion and/or spin-spin interaction. For quantum computing purposes, these results would be termed spin entanglement. One can then expect to easily tune the number of entangled spins via dilution in glassy matrices. SQUID detected EPR techniques have been proposed for spin detection for quantum computing.¹⁵ This work on the pure compound should also serve as a template and base line for investigations of trityls and other magnetic systems as a function of dilution into glassy matrices.

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