The Low Temperature Magnetic Properties of Bulk and Nanoparticle DPPH

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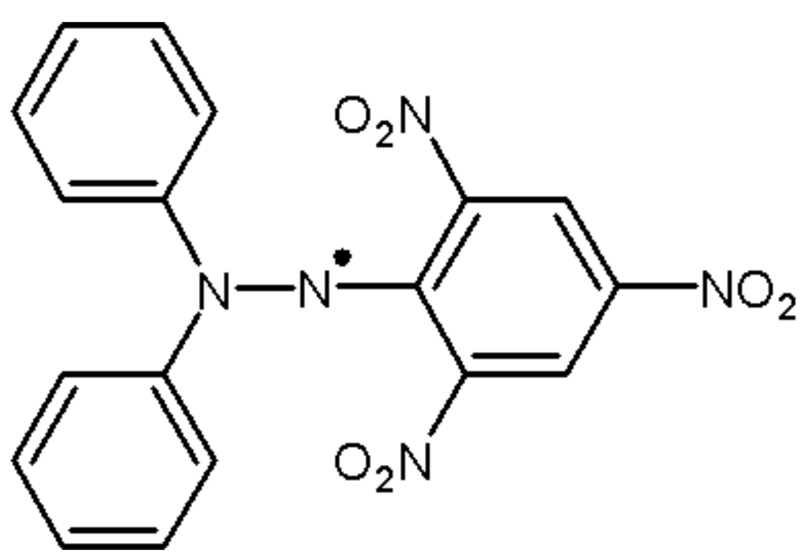
Abstract:

The magnetization of bulk and nanoparticle samples of DPPH [2,2-Diphenyl-1-Picrylhydrazyl] have been measured from 2 K to 300 K in magnetic fields of 100 G. At 2 K, isothermal magnetization studies were performed in fields up to 70 kG. The data and analysis suggest unusual magnetic behavior exists below ~ 15 K. At higher temperatures, the results can be explained by weakly or non-interacting magnetic spins.

Structure:



Introduction:

The free organic radical DPPH in its bulk form with one unpaired electron per molecule (S = 1/2) has been investigated for a long time in many research laboratories [1-4]. The molecule is of interest because of widespread use in EPR (Electron Paramagnetic Resonance) due to its single, narrow resonance line that is used for g-factor determination and magnetic scan calibration [2]. The motivation of this research is to characterize the low temperature magnetic response of nanoparticles (NPs) of DPPH and to contrast those results with the behavior of their bulk counterparts.

DPPH EPR measurements:

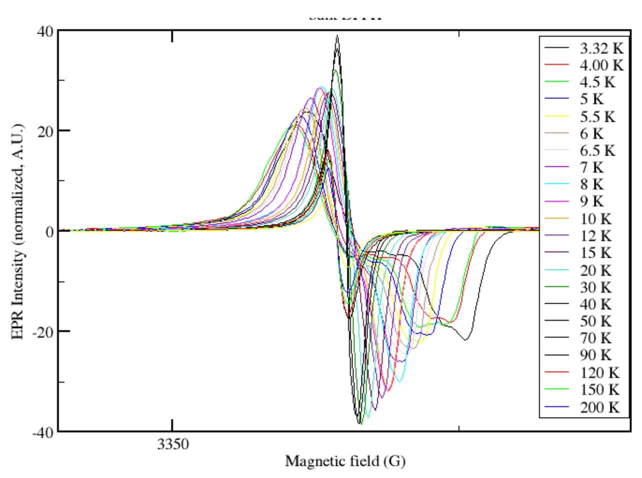


Fig. 5. EPR spectrum of 250 nm DPPH NPs (9.5 GHz).

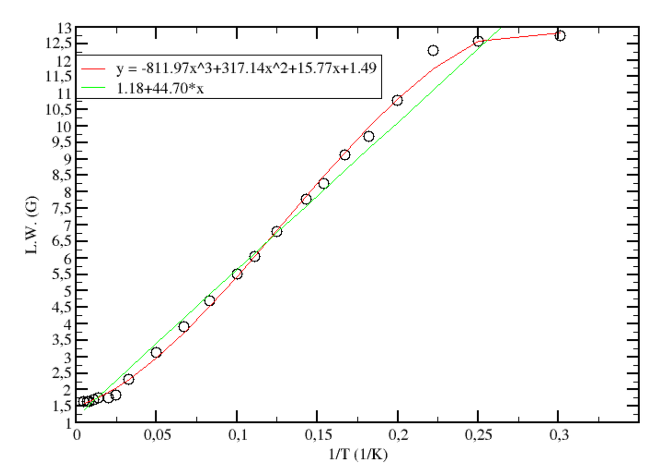


Fig. 6. NP EPR line width (LW) versus temperature inverse .

Experimental methods:

There were two ways used to load DPPH samples for magnetization measurements: in a "can", and sample in a "gelcap". The can is a 0.273 mL polyethylene container with a cover that latches. The gelpcap is a gelatin ~ 0.2 mL capsule. The sample was loaded into its container, which was mounted into a drinking straw that moved through the pickup coils in the magnetometer. First, the sample was centered at (300 K, 0 G) and then centered at (300 K, 100 G) and (300 K, 3 kG).The magnetic properties were studied as a function of temperature, down to T = 2 K, and magnetic field, up to H = 70 kG, by using a Quantum Design magnetic properties measurement system (MPMS). The sample masses were recorded using a Mettler AE163 analytical balance. The molecular weight of DPPH is 394.32 g/ mol.

Susceptibility measurements:

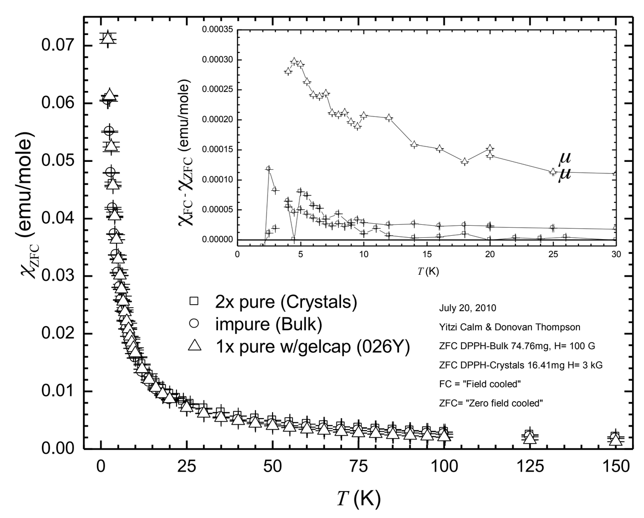


Fig. 1. The temperature dependence of the magnetic susceptibilities in zero field cooled with a constant field of 100 G (bulk) and 3 kG (crystals). The inset shows susceptibilities of field cooled minus zero field cooled.

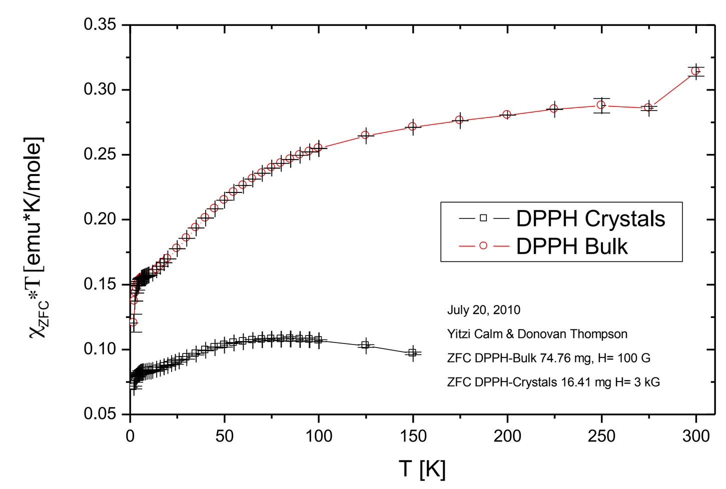


Fig. 2. Zero- field cooled susceptibility-temperature product versus temperature of DPPH with a constant field of 100 G (Bulk) and 3 kG (crystals).

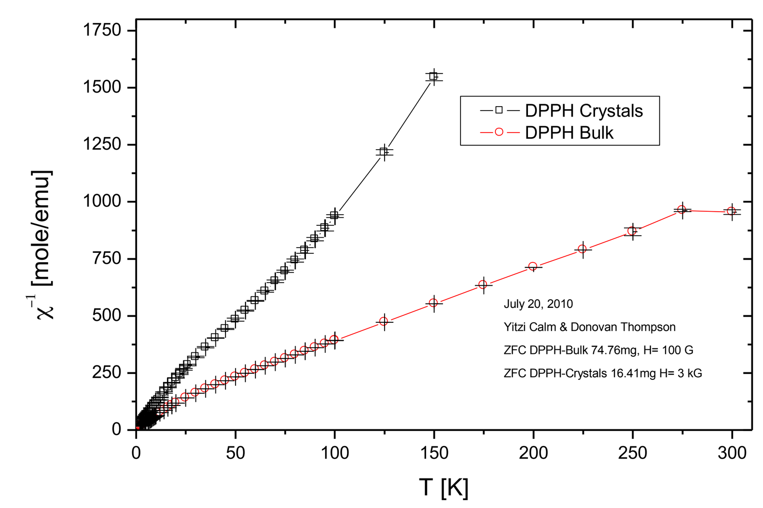


Fig. 3. Zero- field cooled temperature dependence of the susceptibility reciprocal with a constant field of 100 G (Bulk) and 3 kG (crystals).

Magnetization measurement:

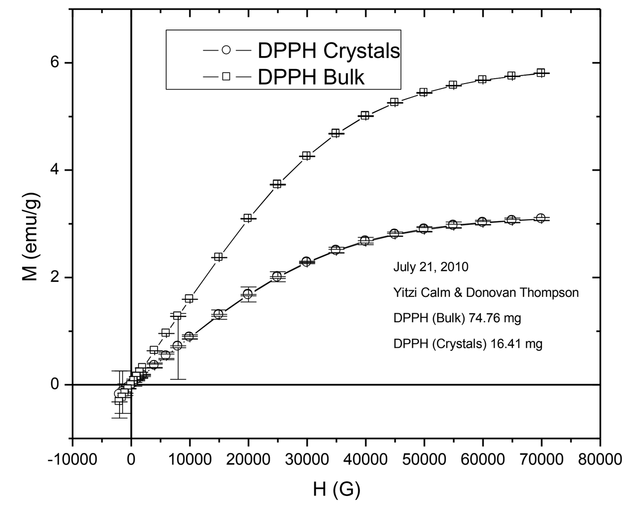


Fig. 4. The field (H) dependence of the magnetization (M) was measured at 2 K.

Bulk DPPH:

The bulk DPPH sample was purchased from Sigma-Aldrich (1898-66-4) and used without further purification.

DPPH Crystals:

DPPH was recrystallized twice from carbon disulfide (CS_2). Typical crystallites were needles of 1 to 2 mm length and 0.1 to 0.2 mm thicken.

Synthesis of DPPH (NPs):

First, DPPH (11 g) was dissolved in THF (2 ml) under Ar to form a deep purple colored stock solution, of which 100 µl was injected into a flask with 5 ml of water (Nanopure, 18.2 MΩ) at room temperature with vigorous stirring. After a predetermined growth time (0-2 h), aqueous gelatin solution (1.8 ml, 2 wt %) was injected into the growth solution, which was kept under stirring for 5 more minutes; the DPPH NPs were then isolated from the growth solution through centrifugation at 15,000 rpm and 20^{o} C [2].

Future work:

DPPH (NPs) will be tested using the SQUID Magnetic Property Measurement System (MPMS) and additional susceptibility measurements are needed to help clarify these interpretations.

Acknowledgements/ References:

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