Muon spin relaxation study of spin dynamics in a polysaccharide iron complex

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Polysaccharide iron complex, a ferritin analog, has been examined with zero-field muon spin-relaxation at temperatures from 2 to 40 K. Spectra exhibit a clear separation of static moments and collective excitations at low temperatures. At intermediate temperatures, superparamagnetic relaxation is observed and a blocking temperature of $T_B = 10 \pm 2.5$ K is measured, in agreement with transmission Mössbauer spectra and frequency dependent χ_{ac} data. Superparamagnetic relaxation rates of 20–150 MHz are in agreement with those extrapolated from Mössbauer spectra using a multilevel magnetic relaxation model.
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I. INTRODUCTION

The basic unit of a fine particle system is a single domain particle. At the lowest temperatures the magnetization direction of the particle will remain fixed along its easy axis, in a blocked state. With increasing temperature, the particle's moment will begin to oscillate around its easy axis, undergoing collective excitations.[1] The thermal energy grows with rising temperature until 180° moment flips occur about the easy axis. The temperature at which moment flips begin is the blocking temperature T_B of the particle. The moment is now superparamagnetic, and its flip rate or relaxation rate, will increase rapidly with rising temperature. In a real system, a distribution of particle sizes and interparticle interactions smear the temperatures at which the transitions from blocked to collective excitations and superparamagnetism occur. Interparticle interactions will affect the anisotropy energies of particle moments and change the temperature at which spin flips will occur. With a distribution of particle sizes, at any given intermediate temperature, moments of large particle will be blocked, intermediately sized particle moments will undergo collective excitations, while the moments from smaller particles will be superparamagnetic.

Characterizing spin dynamics in a real fine particle system hinges upon the ability to clearly separate magnetic relaxation effects from the particle size distribution. Since various measurement techniques are sensitive to different regions of the particle size distribution and T_B is usually defined as the temperature at which the relaxation time and measuring time coincide, comparison of this and other magnetic properties determined by different methods can be difficult. For example, magnetization measurements, with a slow measuring time, are most sensitive to moments from large particles while susceptibility measurements will provide the strongest signal for moments which are oscillating with a rate similar to the ac measuring frequency.

Zero-field experimental techniques are best suited for studying spin dynamics in fine particle systems as there is no external magnetic field which may affect the magnetic behavior of the system. Transmission Mössbauer spectroscopy[2,3] and selective excitation double Mössbauer spectroscopy[4] are such tools, where spin dynamics can be separated from the effects of interparticle interactions and a particle size distribution. Another zero-field experimental technique which offers distinct signals from static and dynamic magnetic moments is muon spin relaxation (μSR) spectroscopy.

The muon is a sensitive local magnetic probe, where zero field μSR (ZF-μSR) provides a Kubo–Toyabe type line shape in the early time channels from static magnetic behavior and an exponential decay in later time channels from spin dynamics. With a relaxation time window which spans several decades, results obtained using μSR can be compared with those from Mössbauer spectra and the relaxation rates of collective exactions can be observed, a phenomena which appears static on the time scale of the Mössbauer effect.

We have examined a polysaccharide iron complex (PIC)[5] with ZF-μSR. Defining spectral features from static moments, collective excitations and superparamagnetic spin flips have established μSR as a useful tool for probing magnetism in fine particle systems. Comparisons with transmission Mössbauer spectra and χ_{ac} data result in the appropriate scaling of T_B with the measuring time. Spin flip relaxation times determined with ZF-μSR are in agreement with our multilevel transmission Mössbauer spectra description.

II. EXPERIMENTAL METHODS

A ferritin analog, the akaganéite based PIC had a mean particle size of 6.5 nm.[6] Basic magnetic characterization was carried out on a commercial susceptometer/magnetometer. ^{57}Fe Mössbauer spectra were obtained on a constant-acceleration spectrometer using a 1 GBq ^{57}Co**Rh** source. Temperatures between 12 K and room temperature were achieved using a vibration-isolated closed-cycle refrigerator. A helium flow cryostat was used to reach temperatures from 2 to 10 K. Mössbauer spectra were fitted using a multilevel relaxation model.[2,3] Zero-field μSR measurements were made on the M20 beamline at TRIUMF. Sample tem-

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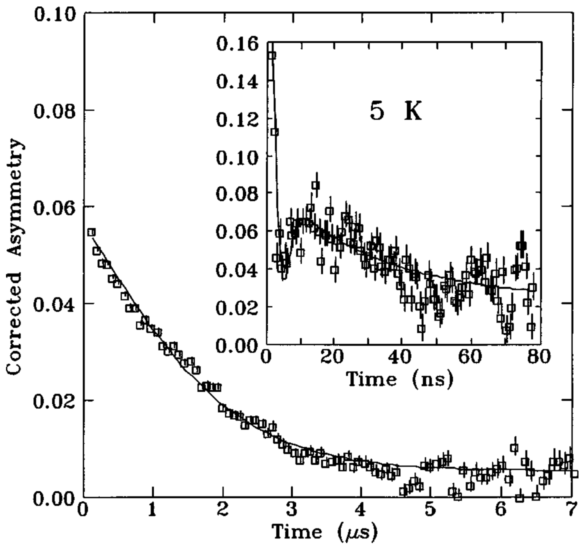

FIG. 1. Typical μSR spectra for PIC at 5 K. Inset shows the early time region of the data where the static KT minimum with fast relaxation is observed. Solid lines are fits to functions.

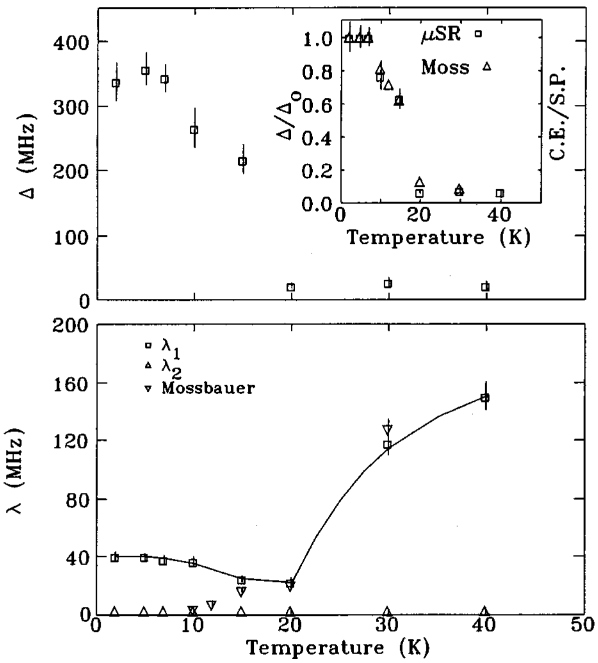

FIG. 2. Temperature dependence of the static (Δ) and dynamic (λ) relaxation rates in PIC. The decrease in Δ and increase in λ indicate when moments begin to unblock at T_B. Notice the similar ratio of moments undergoing collective excitations (CEs) and superparamagnetism (SP) from the Mössbauer model and μSR (Δ/Δ_0) results (inset to top plot) and agreement of relaxation rates from the μSR (□) and transmission Mössbauer fits (△). The solid line is a guide to the eye.

peratures were controlled between 2 and 40 K in a helium flow cryostat. Field zero was set to better than 1 μT using a flux gate magnetometer. Samples were 200 mg cm^{-2} thick over a 16 mm diam active area. Histograms containing $1-4\times 10^7$ events were acquired with a timing resolution of 0.8 ns.

The static order in the samples were fitted using a Kubo–Toyabe (KT) function:[7] $G_z(\Delta)=\frac{1}{3}+\frac{2}{3}[1-(\Delta t)^2]\times\exp(-(\Delta t)^2/2)$ with Δ/γ_μ representing the probability distribution of local fields where γ_μ is the muon's gyromagnetic ratio. Spin dynamics were fitted using a exponential:[8] $A_d=\exp(-\lambda t)$ with λ a spin relaxation rate.

III. RESULTS AND DISCUSSION

Typical μSR spectra for PIC are shown in Fig. 1. Magnetic fluctuations couple to the muon spin and cause an exponential decay of the observed polarization. The inset shows that this exponential decay changes character at early times. A characteristic KT minimum is observed, indicating the presence of static magnetic order. As PIC is a synthetic complex of akaganéite with a carbohydrate shell having an iron content of approximately 50%[6] by weight, it is plausible to expect one contribution from the carbohydrate shell and another contribution to be due to the akaganéite. Muon depolarization from the static moments in the core will result in a KT line shape. Stray field effects from the antiferromagnetic core should be negligible, so the diamagnetic carbohydrate shell will have a small internal field and muon depolarization from the shell should exhibit a temperature independent relaxation.

We have fitted the PIC μSR spectra with the following line shape: $A=A_0\{\zeta A_d(\lambda_1)\times G_z(\Delta)+(1-\zeta)A_d(\lambda_2)\}$ where A_0 is the initial instrumental detector asymmetry and ζ the fraction of the two spectral components. Examining Fig. 1, we see that this accurately models the spectral line shape. A fitted $\zeta=0.53\pm 0.03$ is in agreement with the weight ratio of the ferric and carbohydrate components of PIC. Fit results are shown in Fig. 2. At the lowest temperatures, a large Δ indicates blocked magnetic moments of the larger particles in the PIC. At 10 K, Δ begins to decrease as these moments begin to unblock from thermal fluctuations which cause the average static moment to decrease.[8] After 10 K, a larger fraction of moments begin to unblock until 20 K where the small Δ indicates that all but the largest particles have unblocked.

Spin dynamics at temperatures below 10 K consist of the particle moments in the PIC undergoing collective excitations. These collective excitations result in $\lambda_1\sim 40$ MHz. As the muon is sensitive to a wider range of measuring frequencies, collective excitations, which appear static during the ~10 MHz measuring frequency of the Mössbauer effect, will exhibit dynamic behavior with μSR. This trend is consistent with Mørup's collective excitation model, which assumes that the moment fluctuations are faster than the Mössbauer effect measuring frequency.[1] Additional evidence of collective excitations is demonstrated by the final depolarization of the low temperature spectra not decaying to zero (e.g., Fig. 1). This offset marks the fraction of muons in the magnetic core that are *not* undergoing superparamagnetic relaxation, and decreases with rising temperature as moments begin to fluctuate. When moments begin to unblock at 10 K, a small decrease in the measured relaxation rate of the iron particles occurs. As the number of particle moments that are undergoing superparamagnetic spin flips increases with temperature, the fraction of the depolarization from the superparamagnetic moments becomes larger than the component from moments that are undergoing collective excitations. At ~15 K, more moments are undergoing slow superparamagnetic relaxation then collective excitations, and a small decrease in λ_1 occurs. As more moments become superparamagnetic, λ_1 increases dramatically. The fitted relaxation rates are in good agreement with those used to fit the transmission Mössbauer spectra (Fig. 2). The ratio of moments undergoing collective excitations and those that are superparamagnetic in the particle distribution determined from the μSR data (Δ/Δ_0 where $\Delta_0 = \Delta$ extrapolated to 0 K) and transmission Mössbauer model are in good agreement (see inset to Fig. 2). To compare blocking temperatures between χ_{ac}, Mössbauer and μSR results, it is necessary to establish the measuring time of the muon when moments begin to unblock. From the expression $\tau_m = \lambda/(\Delta/(2\pi))^2$,[7] $\tau_m = 1.3 \pm 0.3 \times 10^{-8}$ s at 10 K. This calculated τ_m and $T_B = 10 \pm 2.5$ K are in excellent agreement with T_B extrapolated from frequency dependent χ_{ac} results and our multilevel transmission Mössbauer model, shown in Fig. 3. Finally, the carbohydrate coating of the PIC results in a slow temperature independent relaxation with $\lambda_2 = 0.58 \pm 0.02$ MHz, consistent with slow dipole moment fluctuations.

IV. CONCLUSIONS

ZF-μSR has been used to examine a magnetic fine particle system. Static moments, collective excitations, and superparamagnetic relaxation have been clearly distinguished in the presence of a distribution of particle sizes. A moment fluctuation frequency of 40 ± 1 MHz for the collective excitations is consistent with Mørup's model. The blocking temperature of 10 ± 2.5 K is in excellent agreement with transmission Mössbauer and χ_{ac} data. Superparamagnetic relaxation rates are in agreement with those used in our multilevel transmission Mössbauer spectra model, confirming the validity of this description.

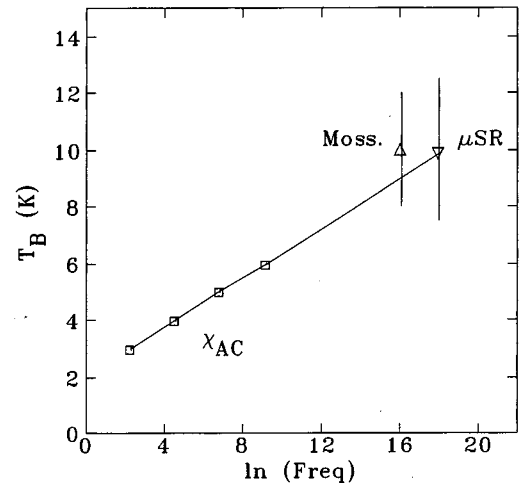

FIG. 3. Plots of T_B vs measurement frequency for the ZF-μSR, χ_{ac} measurements, and Mössbauer multilevel model.

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