Superparamagnetic Spin Dynamics Studied Using Selective Excitation Double Mössbauer Spectroscopy

J. van Lierop and D.H. Ryan

Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada

(September 27, 2000)

A detailed study of spin dynamics in a 6 nm Fe_3O_4 ferrofluid using a substantially improved Selective Excitation Double Mössbauer (SEDM) experimental technique have led to the unambiguous separation of static disorder, collective excitations and moment reversals. Superparamagnetic spin flips have been observed through the appearance of an additional line in the SEDM spectrum, defining the energy transitions during relaxation, with frequencies of 2.5±0.3 MHz at 70 K to 9.7±1.0 MHz at 110 K. SEDM offers a precise window into the dynamics and blocking behavior of fine particle systems.

PACS numbers: 75.50.Tt 76.60.Es 76.80.+y

The basic building block of a superparamagnetic fine particle system is an exchange-coupled assembly of magnetic moments no larger than a single magnetic domain [1]. If, for simplicity, this particle can be described as having a single axis along which the magnetization prefers to lie, then the energy necessary to tilt the moment away from this easy axis by an angle θ can be written as: $E = -KV\cos^2(\theta)$, where K is the anisotropy constant of the particle and V is its volume. At high temperatures, when the thermal energy (kT) is very much larger than the energy barrier KV, the moment can adopt any orientation within the particle and thermal fluctuations cause the average magnetization to be zero. As the temperature is lowered, the continuous tumbling is gradually replaced by 180° moment flips between the two easy directions. With decreasing temperature, the time between these superparamagnetic reversals increases until it is comparable to the measuring time of an experiment; below this temperature, T_B, the moment will appear to be stationary, or blocked. Once $kT \ll KV$, the probability of a magnetization reversal in a given time becomes vanishingly small, and a large particle magnetization is observed. Although no longer superparamagnetic, the moment direction continues to fluctuate about the easy axis, causing the observed particle moment to be slightly reduced. These small amplitude collective excitations can be viewed as the particle moment rocking in its potential well [2]. The amplitude of the collective excitations diminishes with temperature until the particle moment is ultimately frozen along its easy axis and the system is static.

In real fine particle systems, the situation is complicated by the presence of interparticle interactions and a distribution of particle sizes. Interactions arise because particles are generally close enough to be affected by the dipole fields from neighboring particles. These fields tend to cause a reduction in the effective anisotropy, K [3], decreasing T_B and contributing to static magnetic disorder. In addition, any distribution of particle sizes will smear out the simple behavior described above. At any given temperature, the smallest particles will be superparamagnetic, while others undergo collective excitations and the largest particles are essentially static. The blocking temperature becomes more difficult to define in the presence of a broad particle size distribution as various measuring techniques exhibit differing sensitivities to regions of the size distribution. For example, magnetization is dominated by the response of the larger, slower particles, while the majority of the susceptibility comes from particles close to their blocking temperature. A final complication arises from the chemical or grinding procedures used to prepare most fine particle systems. These lead to the introduction of varying degrees of static disorder which can further affect K and also build in a static disorder contribution that can mimic the dynamic disorder that arises from collective moment fluctuations.

In principle, transmission Mössbauer spectroscopy can be used to distinguish the contributions from static disorder, collective excitations and superparamagnetic reversals. However, interplay between the various effects can mean that the deconvolution is not unique. For example, it is possible to obtain fully self-consistent fits to the spectra of Invar, a disordered Fe–Ni alloy, in terms of a purely relaxation based model [4], however no magnetic relaxation effects are in fact present, and the temperature dependence in the spectra is due solely to chemical disorder [5]. When the effects of a broad particle size distribution are included, the problem becomes much worse. A typical solution is to fit the spectra with two broadened static forms: a magnetic component to allow for the larger particles below T_B and a paramagnetic component for the smaller particles that are above T_B. The blocking temperature for the whole sample is then defined as the point where the two components have equal areas [6]. This procedure is unsatisfactory; primarily because it is invalid and generally yields poor fits to the data, but also because the derived blocking temperatures are not consistent with those extrapolated from susceptibility measurements [6] as the temperatures at which the paramagnetic component appears depends on the particle size distribution [7].

We report here data from a modified Mössbauer technique: Selective Excitation Double Mössbauer spectroscopy (SEDM). This method relies on Mössbauer analyzing the radiation re-emitted from the sample following resonant pumping into a selected hyperfine state. Static disorder, collective excitations and moment reversals can be completely distinguished as they each yield a distinct and unambiguous signature. The data presented here on a 6.0 nm magnetite ferrofluid [8], show static disorder at the lowest temperatures (T $\sim$ 20 K), the growth of collective excitations by 40 K, and the clear onset of moment reversals at 54 $\pm$ 3 K.

Fig. 1 shows conventional transmission Mössbauer spectra at various temperatures. At 20 K the moments are static (confirmed below by SEDM) and the six–line pattern is broadened by static disorder. As the temperature is raised, the lines develop an increasing asymmetry, broadening towards the center of the pattern, with the effect being strongest for the outer lines. This behavior is due to collective excitations and can be described using a model originally proposed by Mørup [2]. By 60 K, a central component due to particles undergoing spin-flips is apparent, and the collective excitation description is inadequate. With further temperature increases, the central component grows to dominate the spectrum. If the equal-area criterion is applied to these data, a blocking temperature of 70$\pm$5 K is obtained, in severe disagreement with the extrapolation of frequency dependent χ_{ac} data which yields T_B=55$\pm$2 K [7].

The difficulties in analyzing the data in Fig. 1 derive from the similarity of static and dynamic effects, combined with a distribution of particle sizes. Static disorder leads to broad lines, while collective excitations simply cause *additional* broadening and shifts. When a range of particle sizes are present, a wide range of fluctuation amplitudes will be observed at a given temperature, leading to a further contribution to the line broadening. Once spin-flips start occurring in the smallest particles, the collective excitation model fails. However simple spin-flip models [9] cannot account for the contribution of the larger particles until much higher temperatures are reached ($\mathrm{T} \gg \mathrm{T_B}$) and all of the particles are undergoing spin-flips. As a result, for the region of primary interest around T_B, neither model works. Some of these limitations have recently been eliminated by a many-state relaxation model that includes the effects of a size distribution and correctly describes the crossover from collective excitations to spin-flips [7]. This model yields $T_B = 55 \pm 5$ K, fully consistent with the value extrapolated from χ_{ac} data.

To properly examine a magnetic fine particle system, an experimental technique which can unambiguously separate the effects of static disorder, collective excitations and superparamagnetic spin-flips, is needed. In addition, no external magnetic field which might bias moment orientations and dynamics should be present. These requirements can be met by Selective Excitation Double Mössbauer spectroscopy. In this technique, instead of measuring the absorption as the $\gamma-$energy is swept across a wide range of values (see for example Fig. 1), the sample is pumped at a fixed, single energy, and the re-emitted radiation is analyzed.

Long counting times, energy calibration difficulties and instrumental unreliability have resulted in limited use of SEDM since its discovery [10–12]. We have resolved many of these problems by employing a small, transducer-mounted conversion electron detector (CED) containing a 99% ^{57}Fe enriched stainless steel foil [13], as our energy detector. The CED is a much more efficient means of energy detection and yields a much greater signal to background ratio than the conventional approach of Doppler shifting a single line absorber in front of a proportional counter. In addition, specialized digital circuitry ensures a consistent energy calibration and phase-locks the motion of the two transducers, eliminating interruptions for the bi-weekly energy calibrations previously employed. As a result, our spectrometer runs continuously, and combined with the greatly improved performance of the CED, our system yields a one thousand- [10] to five thousand- [11] fold improvement in effective counting time when compared with previous experimental configurations. This makes SEDM a practical technique for use in the study of magnetic relaxation effects.

The SEDM data shown in Fig. 2 were obtained using a modest 1 GBq ^{57}Co**Rh** source. The left-most line in the spectrum was pumped as it has the largest absorption cross-section, thus maximizing the signal and reducing collection times. Sample temperatures of 20 to 200 K were obtained with a closed cycle refrigeration system. Typical counting times were 20 days.

The static magnetic field present at the ^{57}Fe nucleus in a magnetically ordered material induces hyperfine splittings in the $\mathrm{I_g}$=1/2 ground state and the $\mathrm{I_e}$=3/2 excited state. Selection rules ($\Delta \mathrm{m_I}$ =0, $\pm$ 1) mean that only six of the possible eight transitions are allowed, and a six–line spectrum is observed by transmission Mössbauer spectroscopy (see for example the 12 K spectrum in Fig. 1). The left–right symmetry in the spectrum means that the sign of the magnetic field cannot be determined and so superparamagnetic spin flips, which involve a sign reversal in the field, cannot be observed directly. By contrast, the state–specific pumping used in SEDM explicitly breaks this symmetry. If the constant velocity drive is set to an energy corresponding to the leftmost line in the 12 K spectrum in Fig. 1, then the m_{I_g}=–1/2→ m_{I_e}=–3/2 transition is driven and the m_{I_e}=–3/2 excited state is populated. The selection rules allow only a single transition from the m_{I_e}=–3/2 state, and so in a material with a unique, static field, e.g. $\alpha-$Fe, the radiation re-emitted when the excited nucleus returns to the ground state is at the same energy as the pump, and SEDM yields a single sharp line at the pump energy. Static disorder leads to a broadened absorption line and the re-emitted radiation reflects a convolution between the source linewidth and the hyperfine field distribution. A broader re-emission line is observed. However this line can be substantially narrower than that observed by transmission as only part of the distribution is probed [5]. A typical static SEDM spectrum is shown at the bottom of Fig. 2 for the ferrofluid studied here at 20 K.

The onset of magnetic fluctuations has a significant impact on the SEDM spectrum. As collective excitations develop, the SEDM line broadens visibly (compare the 20 K and 50 K SEDM spectra in Fig. 2). However, it is superparamagnetic spin-flips that have the most dramatic effect: at 70 K a new line is clearly present in the SEDM spectrum. This line at ∼+8 mm/s, is due to the m_{I_e}=+3/2→ m_{I_g}=+1/2 transition, and is present even though we have explicitly populated only the m_{I_e}=–3/2 excited state. This is possible because when a spin flip occurs in a particle in which we have pumped a nucleus into the m_{I_e}=–3/2 excited state, the field within that particle reverses, the projection of I_e onto that field changes sign and the populated state becomes m_{I_e}=+3/2. This state then decays to give the line at ∼+8 mm/s. The observation of a *sharp* line at +8 mm/s, indicates that the moment reversal is instantaneous on the timescale of the SEDM measurement. This observation is consistent with estimates that the duration of the moment reversal process is ∼0.1 nm [14], much shorter than the time between reversals (∼100 ns). The intensity ratio of the lines at ∼ –8 mm/s and ∼+8 mm/s is related to the probability that a spin flip occurs during the lifetime of the excited state and is thus a direct indication of the rate at which spin flips happen. We emphasize that no amount of *static* disorder can lead to the appearance of this additional line. It can only be caused by 180° magnetization reversals.

To develop a quantitative description of the SEDM spectra, a model is needed. Using Sack's [15] stochastic quantum mechanical formalism, we have modeled both SEDM and transmission Mössbauer spectra. Transitions between two excited states have been used to describe the SEDM spectra, with the linewidth and relaxation rate as free parameters in a least-squares fit.

Results of fits to the data are shown in Fig. 3. A comparison between the observed linewidths and those obtained with an $\alpha-$Fe foil (dashed line in Fig. 3) clearly shows the effects of static disorder. The further increase in width above 30 K is due to collective excitations. This can be confirmed by treating the data at each temperature in Fig. 1 as broadened solely by a static hyperfine field distribution and using the derived distribution to fit the corresponding SEDM spectrum. While this procedure has been shown to work for purely static systems [5], it fails here, yielding lines that are too narrow. This mis-fit provides further evidence of the presence of collective excitations, and demonstrates that SEDM can be used to distinguish static and dynamic sources of line broadening.

Superparamagnetic spin flips occur with increasing frequency above T_B, going from 2.5 ± 0.3 MHz at 70 K to 9.7 ± 1.0 MHz at 110 K. A blocking temperature of T_B = 54 ± 3 K is extrapolated from a linear fit to the SEDM relaxation frequency, in excellent agreement with transmission Mössbauer and frequency dependent χ_{ac} extrapolations of T_B [7]. The continued increase in fitted linewidth above 80 K as the relaxation frequency increases indicates that our model is too simple, as a correct description of the superparamagnetic processes should involve no linewidth variations. A distribution of relaxation frequencies for each moment size was used in a multi-level relaxation model to fit the ferrofluid transmission Mössbauer spectra [7]. Since transmission experiments are most sensitive to flip rates at or above the Larmor frequency and SEDM is sensitive to flip rates at or below the Larmor frequency, relaxation rates within the time scale of the SEDM measurement were used to fit the SEDM spectra in Fig. 2. The results in Fig. 3 show that a more consistent linewidth was obtained. This agreement between the two experiments strongly supports our description of the transmission Mössbauer spectra of fine particle systems.

In summary, substantial improvements to SEDM methodology have allowed us to characterize the defining magnetic phenomena of a fine particle system. At the lowest temperatures, moments are frozen along their easy axes and the material is easily described by a distribution of static magnetic fields from, for example, chemical disorder and dipole interactions. Collective excitations appear by 50 K and lead to significant, temperature dependent line broadening that exceeds that predicted by a static hyperfine field distribution. Clear evidence of moments undergoing a transition from collective excitations to superparamagnetism is given by the 70 K SEDM spectrum. The additional line is unequivocal evidence that moments are undergoing simple 180° spin-flips and that no other moment orientation process is responsible for the superparamagnetic behavior of these particles. Furthermore, the sharp lines indicate the the reversal is abrupt. Relaxation frequencies of 2.5 MHz to 10 MHz at temperatures of 70 K to 110 K exhibit a gradual increase with temperature. Relaxation rates were measured directly without appealing to models of magnetic excitations, and are not influenced by particle size distributions.

Although collection times remain long, they are comparable to those necessary when using CEDs to study thin films and could easily be reduced by using a more intense source. With the unique ability to decouple static and slow dynamic magnetic effects, SEDM proves to be an ideal technique to the distinguish the effects of interacting particles upon the blocking temperature.

We would like to acknowledge discussions with N. de Takacsy (McGill) during the development of the SEDM model. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and Fonds pour la formation de chercheurs et l'aide à la recherche, Québec.

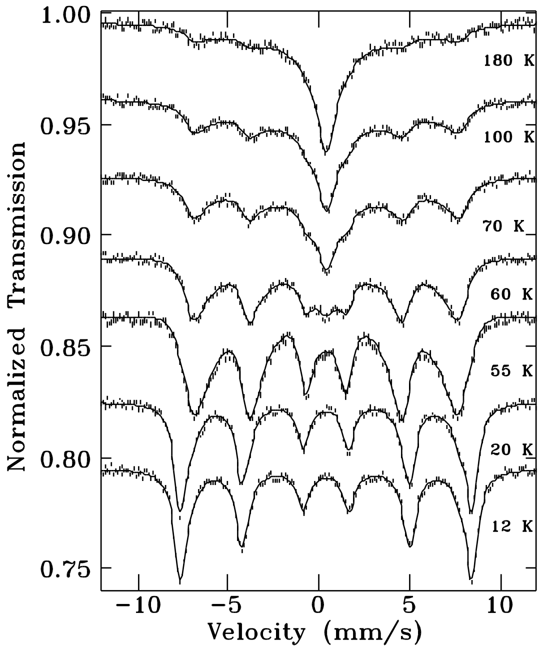

FIG. 1. Typical transmission Mössbauer spectra of a 6.0 nm Fe_3O_4 ferrofluid. Solid lines are fits using a multi-state relaxation model with a distribution of particle sizes [7].

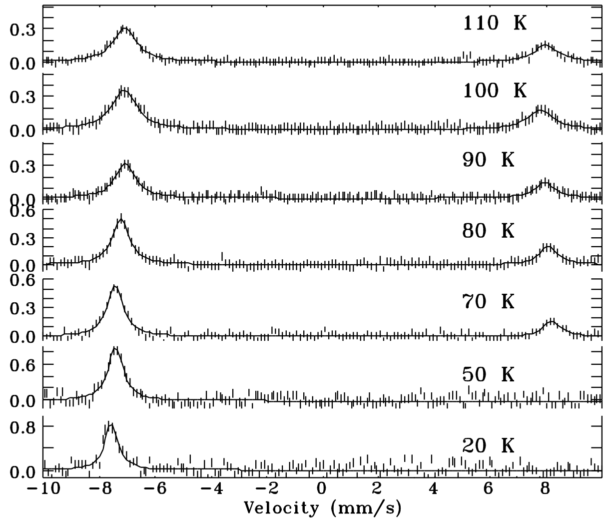

FIG. 2. SEDM spectra of a 6.0 nm Fe_3O_4 ferrofluid. At each temperature, the pump energy was centered on the line at the left. The appearance of the peak at positive velocities indicates the onset of superparamagnetic moment reversals.

[1] J.L. Dormann, D. Fiorani and E. Tronc, in "*Advances in Chemical Physics*", **XCVIII**, eds. I. Prigogine and Stuart A. Rice (John Wiley & Sons, Inc.), 283 (1997).
[2] S. Mørup, J. Magn. Magn. Mater. **37**, 39 (1983).
[3] M.F. Hansen, S. Mørup, J. Magn. Magn. Mater. **184**, 262 (1998).
[4] D.G. Rancourt, H.H.A. Smit and R.C. Thiel, J. Magn. Magn. Mater. **66**, 121 (1987).
[5] J. van Lierop and D.H. Ryan, J. Appl. Phys. **85**, 4518 (1999).
[6] E. Tronc, P. Prené, J.P. Jolivet, F. D'Orazio, F. Lucari, D. Fiorani, M. Godinho, R. Cherkaoui, M. Nogues. J.L. Dormann, Hyp. Int. **95**, 129 (1995).
[7] J. van Lierop and D.H. Ryan, J. Appl. Phys. **87**, 6277 (2000).
[8] Ferrofluidics Corporation, 40 Simon Street Nashua, N.H., U.S.A., 03061.
[9] M. Blume and J.A. Tjon, Phys. Rev. B **33**, 7421 (1968).
[10] Neil D. Heiman and J.C. Walker, Phys. Rev. **184**, 281 (1969).
[11] Bohdan Balko and Gilbert R. Hoy, Phys. Rev. B **10**, 36 (1974).
[12] D.C. Price and A.M. Stewart, Hyp. Int. **42**, 1157 (1988).
[13] L.X. Liao, D.H. Ryan and Z. Altounian, Rev. Sci. Instrum. **64**, 679 (1993).
[14] D.H. Jones, K.K.P. Srivastava, J. Magn. Magn. Mater. **78**, 320 (1989).
[15] R.A. Sack, Molec. Phys. **1**, 163 (1958).

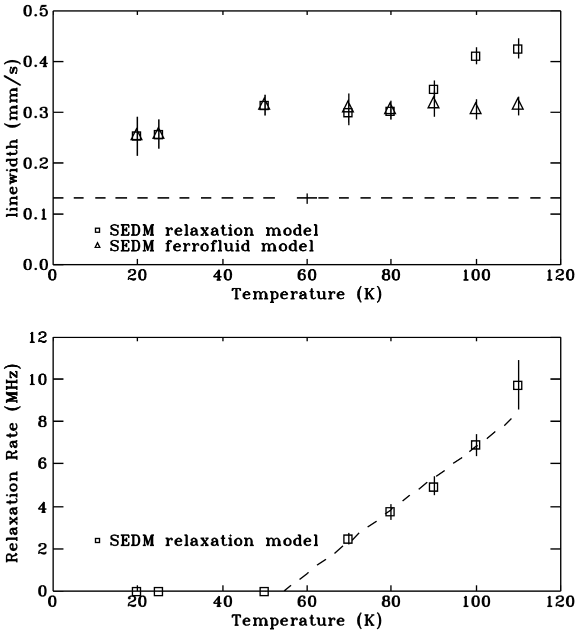

FIG. 3. Results of fits to the data in Fig. 2 using two SEDM models. Top: Linewidth (the dashed line shows the linewidth obtained by SEDM on α-Fe). Bottom: Relaxation rate showing the onset of superparamagnetic spin-flips above T_B=54±3 K.