Muon spin relaxation study of exchange biased Co/CoO

J. van Lierop* and H.S. Isaacs
Materials Science Department, Brookhaven National Laboratory, Upton, N.Y., 11973

D.H. Ryan, A. Beath, and E. McCalla
Physics Department and Centre for the Physics of Materials, McGill University, 3600 University St., Montreal, Quebec, H3A 2T8, Canada

The local magnetic properties of an exchange biased Co/CoO nanoparticle system have been examined using zero-field muon spin relaxation (ZF-μSR) spectroscopy. A direct measure of magnetic domains experiencing the exchange coupling due to the ferromagnetic core and antiferromagnetic shell of the Co nanoparticles is given by the observation of an oscillating signal in the field-cooled ZF-μSR spectra that is a clear and unambiguous signature of static magnetic correlations. Excellent agreement between the local field determined from the μSR oscillation and the bulk exchange bias loop shift confirms this interpretation. Furthermore, the unique lineshape and increase in moment fluctuation rate on cooling the exchange biased sample is a strong indication that spin-density wave like behavior is associated with setting the exchange bias in this system. This static field oscillation is likely due to the twisted moment directions at the interface.

PACS numbers: 75.70-i, 75.50.Tt, 75.75+a, 76.75+i, 75.70.Cu

I. INTRODUCTION

Exchange coupling at the interface between a ferromagnet and antiferromagnet leads to unidirectional anisotropy, commonly observed as a loop shift of the magnetization curve away from the zero field axis when a system has been field-cooled from above its Néel temperature (T_N). This loop shift is believed to arise from order in the antiferromagnet being established in the presence of the ferromagnet. The antiferromagnet is weakly coupled to external fields so that its magnetization retains its direction even when the ferromagnet's magnetization is later rotated. The torque at the interface results in the loop shift, referred to as exchange bias[1–3].

Since the essential behavior of exchange bias depends critically on the atomic-level chemical and spin structure at the interface between the ferromagnetic and antiferromagnetic components, we have applied muon spin relaxation (ZF-μSR), an exquisitely sensitive local magnetic probe to a compact of partially oxidized Co nanoparticles ($\sim$ 7 nm), the archetypical exchange biased system. ZF-μSR allows us to probe the local magnetism in a way that is closer to the conditions used in theoretical models of exchange biased materials[2,3], unparalleled by the usual bulk magnetic measurement techniques.

The static and dynamic magnetic behavior has been examined as a function of temperature both in the as-prepared state, and following exchange coupling by field cooling from above T_N. In the as-prepared state, the temperature dependence of the μSR data is essentially the same as that observed in other ZF-μSR studies of magnetic fine particle systems[4]. However, establishing exchange coupling between the ferromagnetic Co core and the antiferromagnetic CoO shell by field-cooling the sample (in the direction parallel to the muon beam) through T_N and then removing the field, drastically alters the ZF-μSR spectra. In addition to the nature of the static magnetic field distribution observed in the original data changing, there is prominent large amplitude oscillation (Fig. 1) that is ascribed to the field at the interface between the ferromagnet and antiferromagnet. Furthermore, in contrast to the zero-field cooled data where the measured moment fluctuation rate decreases with cooling (typical time-dependent magnetism for a fine particle system), the field-cooled data shows an *increase* in the local moment fluctuation rate on cooling. This increase of the relaxation rate of the magnetic moments in the Co/CoO nanoparticles with decreasing temperature, combined with the drastic change in μSR lineshape[5]) points towards spin-density wave like behavior being established when exchange bias is set. This measured static field oscillation that establishes the spin-density wave is likely due to the twisted moment directions at the ferromagnetic/antiferromagnetic interface.

II. EXPERIMENTAL METHODS

The sample of partially oxidized Co nanoparticles was prepared by dealloying[6] 50 wt.% AlCo in a 20 wt.% NaOH solution at $\sim$ 370 K following the same recipe that is used to make Raney Ni[7]. The Co powder was then washed several times with distilled water until the wash water showed neutral pH, and let dry in air. Cu K-α x-ray diffraction data collected on a conventional automated powder diffractometer show strong Co and CoO peaks and low intensity Co_3O_4 peaks[8], and Scherrer analysis of the peak widths indicate a mean particle size of $\sim$ 7 nm. Basic magnetic characterization was carried out on a commercial susceptometer/magnetometer. ZF-μSR measurements were made on the M20 beamline at TRIUMF with the LAMPF rig. The sample was $\sim$ 200 mg/cm^2 thick over a 16 mm diameter active area. Sample temperatures were controlled between

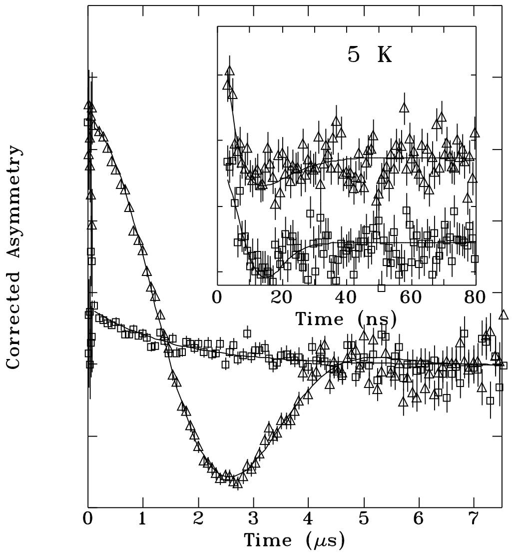

FIG. 1: Typical as-prepared (□) and field-cooled (△) ZF-μSR data at 5 K. Inset shows the early time region of the data. Solid lines are fits to functions described in the text.

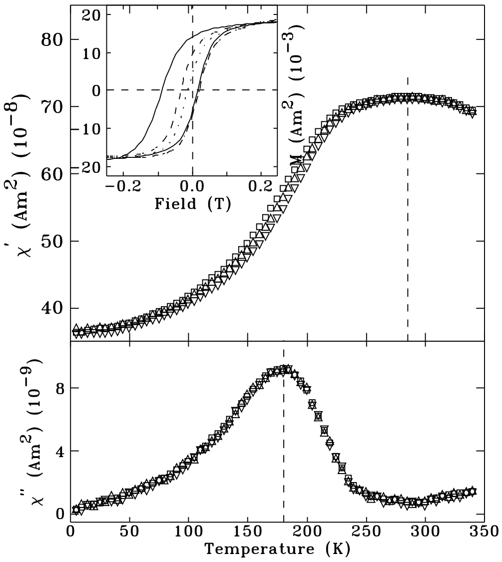

FIG. 2: In-phase (χ') and out-of-phase (χ'') AC susceptibility data at 10, 100 and 1000 Hz with a 0.375 mT field for the Co/CoO nanoparticle system. Inset shows 250 mT field-cooled M vs B_o loops at 5 K (solid line), 100 K (dashed line) and 175 K (dotted line). The 5 and 100 K loops clearly show an exchange bias loop shift.

5 and 250 K in a helium flow cryostat. A 225 mT field was applied (with a water-cooled Cu wire solenoid) to the sample in the direction parallel to the muon beam for the 300 to 5 K field-cooled ZF-μSR measurements. Field zero was set to better then 1 μT using a flux gate magnetometer. A pure silver (99.99%) mask prevented stray muons from striking any of the mounting hardware. Histograms containing $1-4\times10^7$ events were acquired with timing resolutions of 0.625 ns. The time-dependent asymmetry was then fitted using a conventional nonlinear least-squares minimization routine.

III. RESULTS AND DISCUSSION

Fig. 2 shows the in-phase (χ') and out-of-phase (χ'') AC susceptibility data for the Co/CoO nanoparticle system as well as some sample 250 mT field-cooled magnetization (M) vs field (B_0) loops at 5, 100 and 175 K. The broad $\chi'(T)$ peak at high temperatures where the three measuring frequencies result in the same χ' values denotes the $T_N = 285 \pm 10$ K of the CoO nanoparticle shells, in good agreement with the T_N of CoO[1]. At lower temperatures there is a small spread in the $\chi'(T)$ values for the different drive frequencies. This spread is attributed to moments from larger single domain particles undergoing superparamagnetic fluctuations slowing with cooling and becoming static before the moments of smaller particles[9]. This behavior is due to the inevitable distribution of particle sizes in the sample. Additional evidence of a $T_N \sim 285$ K is marked by a minimum in $\chi''(T)$ at high temperatures. Most interesting is a broad peak in the $\chi''(T)$ data centered at 175 ± 5 K that seems to mark the onset of exchange bias in the nanoparticle system. Looking at the loop shift (H_E) values shown in Fig. 3, we see that the exchange bias starts at 175 K, in excellent agreement with the $\chi''(T)$ peak position. The broad width of the $\chi''(T)$ peak is further indication that there is a range of temperatures where the moments from different sized particles change from superparamagnetic to static with cooling. 175 K marks the temperature where the majority of moments are static (i.e. the average exchange energy of the system is greater then the thermal energy) so that exchange bias can occur. The gradual decrease of $\chi''(T)$ with cooling is a sign of strengthening exchange coupling between the Co core and CoO shell, mirrored in an increase of $H_E(T)$ (Fig. 3).

Field cooled M vs B_0 loops shown in the inset to Fig. 2 are typical of partially oxidized Co nanoparticle systems[1,10,11]. Measured exchange bias loop shifts as a function of temperature ($H_E(T)$) are shown in Fig. 3 (□). The temperature that the loop shift appears ($H_E > 0$ at $\sim$ 175 K), marking the average blocking temperature of the system, is lower then the measured $T_N \sim 285$ K from the $\chi'(T)$ data, typically a necessary condition to set exchange bias. The H_c (◯) vs $T^{\frac{1}{2}}$ trend shown in the inset of Fig. 3 (dashed line) indicates the presence of some superparamagnetism[11,12] in the material, not surprising considering the small average particle size indicated by the x-ray diffraction measurement, and in agreement with the spread in $\chi'(T)$ as a function of measuring frequency at intermediate temperatures (Fig. 2) as well as the broad $\chi''(T)$ peak as described above.

Many excellent descriptions of ZF-μSR exist (e.g. Ref.[13]), so for the purposes of the analysis described here

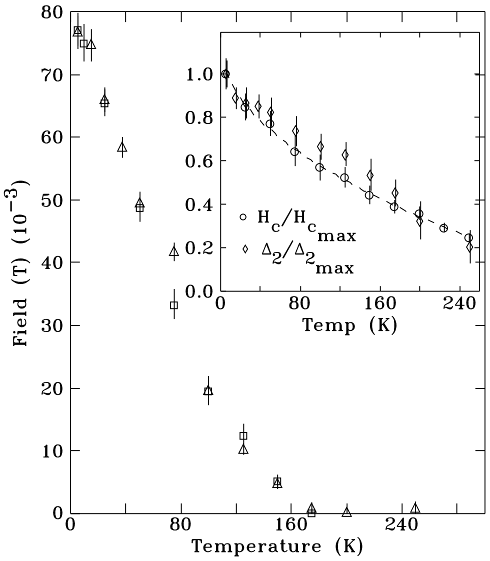

FIG. 3: Loop shift (H_E) values determined from 250 mT field-cooled M vs B_0 loops of the Co/CoO nanoparticle system as a function of temperature (□) and calculated static field measured from the large amplitude oscillation in the field-cooled ZF-μSR data. Inset shows the temperature variation of the normalized H_c and Δ_2 fitted from the M vs B_0 loops and field-cooled ZF-μSR data respectively (there is an artificial temperature offset to help distinguish between the H_c and Δ_2 data) . Dashed line is a fit described in the text.

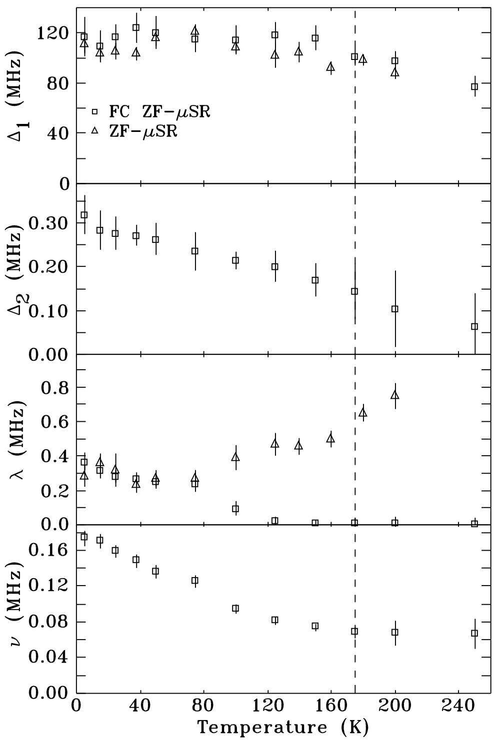

FIG. 4: Temperature dependence of the fitted static (Δ), dynamic (λ) and large amplitude oscillation (ν) representing the static interfacial field of the zero-field and field-cooled ZF-μSR data. Dashed line at 175 K marks where $H_E > 0$ from the M vs H loops.

we will note only the following. If a muon comes to rest at a site with a local field B_x, then the muon spin will precess about the field at the Larmor frequency $f_L = B_x\gamma_\mu$ ($\gamma_\mu = 0.1355$ MHz/T)[14]. This precession leads to a periodic oscillation of the observed asymmetry. The material studied here is both structually disordered and magnetically disordered as a result of exchange bias, therefore we expect a distribution of local fields to be present. This is clearly shown in the typical ZF-μSR spectra of the as-prepared and 225 mT field-cooled sample shown in Fig. 1. For the as-prepared ZF-μSR data, the muon depolarization was fitted with

$$G_z(t) = \{\frac{1}{3}+\frac{2}{3}[1-(\Delta t)^\alpha]\exp(-\frac{(\Delta t)^\alpha}{\alpha})\}\times\exp(-\lambda t) \quad (1)$$

where for $\alpha = 1$ the term in $\{\cdots\}$ denotes a Kubo-Toyabe (KT) asymmetry form for a Lorentzian distribution of static local fields[14] and for $\alpha = 2$ the term in $\{\cdots\}$ is the KT asymmetry form for a Gaussian distribution of static local fields with Δ/γ_μ the rms field. λ represents a $1/T_1$-type spin relaxation rate. The field-cooled ZF-μSR data were fitted with a phenomenological form inspired by μSR studies of the $(TMTSF)_2-X$ compounds that exhibit spin-density waves[5]. The only functional form that would consistently describe the full temperature range of the μSR data was

$$\begin{aligned} G_z(t) = {} & A_1\{\tfrac{1}{3}+\tfrac{2}{3}[1-(\Delta_1 t)]\exp(-\Delta_1 t)\}+ \\ & A_2\{\tfrac{1}{3}+\tfrac{2}{3}[1-(\Delta_2 t)^2]\exp(-\tfrac{(\Delta_2 t)^2}{2})\times \\ & \exp(-\tfrac{(\lambda t)^2}{2})\times\cos(2\pi\nu t+\phi)\} \end{aligned} \quad (2)$$

Δ and λ describe the static and dynamic fields respectively, while ν marks the single static field from the late time depolarization in the μSR spectra.

Results of fits to the ZF-μSR data are shown in Fig. 4. For the as-prepared ZF-μSR spectra, a Gaussian distribution ($\alpha = 2$ in Eqn. 1) of static fields described the early time data, similar to other μSR studies of magnetic fine particle systems[4]. We find that there is a slight increase in the average static field when cooling below 200 K (Δ_1(△)), behavior that is consistent with moment fluctuations in the Co slowing and becoming static on the time-scale of the muon[4]. This slowing of the spin dynamics with cooling is more clearly seen in the $\lambda(T)$ behavior (Fig. 4, △) that describes the late-time slow exponential decay of the observed muon depolarization. From 200 K down to $\sim$ 75 K there is a gradual decrease in the moment fluctuation rate, λ. This trend has been observed in μSR and Mössbauer studies of magnetic fine particle systems[4] and linked to a measured decrease in the superparamagnetic component of the μSR signal, and we ascribe the $\lambda(T)$ behavior in the partially oxidized Co sample to the same phenomena. The settling of $\lambda(T)$ to a essentially constant value below 75 K is due to spin dynamics changing from 180° moment flips to collective magnetic oscillations[4].

For the field-cooled ZF-μSR fits (Eqn. 2), $A_1 = 0.085 \pm 0.006$ and $A_2 = 0.059 \pm 0.006$, so the two spectral components were well decoupled for all temperatures, and the fitted phase shift ($\phi = 0.01 \pm 0.04$) was essentially zero for all temperatures. For all temperatures, the early time region (A_1) of the spectra (Fig. 1, $\triangle$) was well described by a Lorentzian distribution of static fields ($\alpha = 1$). This is in contrast to the Gaussian distribution of static fields ($\alpha = 2$) that fitted the as-prepared μSR data described above. Evidently the exchange coupling between the ferromagnetic Co core moments and the antiferromagnetic CoO shell moments that was established when the sample was field-cooled from 300 K has drastically affected the nature of the static local field distribution. Although the nature of the field distribution has changed, we see that the magnitude of the static field itself is essentially unaltered ($\Delta_1(T)$ ($\square$) shows the same trend as $\Delta(T)$ ($\triangle$)). This underlines the importance of using an atomic level local probe technique on exchange biased materials since bulk magnetic measurements are sensitive only to the strength of the exchange bias field, and not to the nature of the field distribution. This focusing of the local magnetic field distribution from Gaussian to Lorentzian is not present (to our knowledge) in any of the theories of exchange bias[2,3], and indicates that ferromagnetic-antiferromagnetic coupling for exchange bias produces a more dilute magnetic system[13,14].

The similarities between the as-prepared and field-cooled ZF-μSR spectra end in the later time regions. As is clearly seen in spectra shown in Fig. 1, there is a striking change in the later-time muon depolarization when the sample is field cooled ($\triangle$). The second (A_2) component of the fitting function (Eqn. 2) is necessary to describe this part of the μSR spectra. A Gaussian distribution of small static fields (Δ_2 in Fig. 4) coupled with a single static field (ν) that marks the strong oscillation in the depolarization data is necessary to fit the μSR data from 260 to 125 K. This static field oscillation is likely due to the twisted moment directions at the ferromagnetic/antiferromagnetic interface that allows the local field distribution to vary. Below 125 K, the late-time data exhibits a weak exponential decay that is of the same magnitude as that fitted from the lower temperature as-prepared data described above (Fig. 4, $\triangle$). However, unlike that data which shows a trend typical of spin dynamics in a fine particle system, the relaxation rate (λ) *increases* with cooling, and the distribution of fluctuation moments has changed character as well. The nature of the decay has changed from $\exp(\cdots)$ to $\exp(\cdots)^2$.

Changes in the field-cooled ZF-μSR data can clearly be linked to fixing exchange bias (evident through the M vs B_0 results in Figs. 2 and 3). Although the A_1 part of Eqn. 2 is plainly due to the local magnetism of the Co nanoparticles (as it is in perfect agreement with the as-prepared μSR results), the A_2 component describing the results of field-cooling the sample tracks with the temperature dependent magnetism set by the exchange bias. Comparing the temperature variation of the normalized H_c from the M vs B_0 loops and the normalized Δ_2, shown in the inset to Fig. 3, we see there is excellent agreement. This is a strong indication that this part of the ZF-μSR signal is tracking the magnetism set by the interfacial exchange coupling between the ferromagnetic core and antiferromagnetic shell in the particles. Examining $\nu(T)$ in Fig. 4, we see that for temperatures where $H_E = 0$ (i.e. above $\sim$ 175 K) $\nu(T)$ is constant. Treating this as an offset to the lower temperature $\nu(T)$ values (i.e. below $\sim$ 175 K), and subtracting it from the lower temperature $\nu(T)$, we find that the resulting magnetic field measured by the muon, $(\nu/2\pi)(1/\gamma_\mu)$, is in remarkable agreement with the exchange bias field measured via the magnetization data (Fig. 3). The muons are clearly sensitive to the exchange field set by field-cooling the sample in a direction parallel to the muon beam. However, μSR cannot discern between the different possible spin configurations at the interface (e.g. parallel to perpendicular or parallel to anti-parallel), and due to the disordered nature of the nanoparticles, the different interfacial oxides (e.g. the CoO or Co_3O_4) do not present distinct signals. It is interesting to note that at temperatures above where bulk techniques measure $H_E > 0$, there seems to be a constant interfacial field present, implying that some sort of balance between exchange and thermal energies is present, behavior that has been predicted by theory[2,3], and inferred from a general trend of the measured increase of H_c in exchange biased ferromagnetic/antiferromagnetic bilayers compared to a single ferromagnetic layer of equal thickness[2]. Concomitant to this unique $\nu(T)$ behavior is the spin dynamics reflected in the μSR spectra. Fig. 4 shows that on cooling the sample, the moment fluctuations increase in frequency (λ ($\square$), with a very different local field distribution, $\exp(\cdots)$ to $\exp(\cdots)^2$). This is atypical behavior for a magnetic fine particle system[4]. However, this trend has been observed in the low temperature ZF-μSR spectra of materials that exhibit spin-density waves[5,15]. The unprecedented $\nu(T)$ and $\lambda(T)$ behavior, coupled with the unique μSR lineshape of this fine particle system, provide dramatic evidence that spin-density wave like behavior is associated with the setting of exchange bias.

IV. CONCLUSIONS

In summary, the observation of an oscillating signal in the field-cooled ZF-μSR spectra is a clear and unambiguous signature of static magnetic correlations that are tied to the measured exchange bias in the sample. This is confirmed by the fitted Δ_2 and ν temperature behavior. Furthermore, the increase of the measured moment fluctuation rate, λ, with decreasing temperature and resulting μSR lineshape points towards a spin-density wave like phenomenon being associated with exchange bias. The measured static field oscillation is likely due to the twisted moment directions at the ferromagnetic/antiferromagnetic interface that allows the local field distribution to vary. This is a direct measure of the fundamental interface behavior, and is in excellent agreement with the present interfacial coupling picture previously inferred from bulk magnetic measurements and presented by theory[1–3]. As a single large amplitude oscillation is sufficient to describe the μSR spectra when exchange bias is set, we can infer that the interface from ferromagnetic to antiferromagnetic spins is very uniform throughout, as one would expect a range of oscillations with different frequencies (hence different fields) present for a more gradual shift of moment direction from ferromagnetic to antiferromagnetic spins. The above magnetic behavior, in addition to the focusing of the local static field distribution with the setting of exchange bias and the subsequent marked change in the nature of the spin dynamics, indicates that the local magnetism, while sharing may attributes of the bulk (shown by the excellent agreement between the measured static fields and the loop shifts as a function of temperature) is quite complex.

Acknowledgments

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, Fonds pour la formation de chercheurs et l'aide à la recherche, Québec, and in part under the auspices of the U.S. Dept. of Energy, Office of Basic Energy Sciences under contract No. DE-AC02-98CH10886.

---

* University of Michigan Department of Physics, 500 E. University Ave., Ann Arbor, Michigan 48109-1120

1 W. H. Meiklejohn and C. P. Bean, Phys. Rev. **105**, 904 (1957).
2 A. E. Berkowitz and K. Takano, J. Magn. Magn. Mater. **200**, 552 (1999).
3 J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
4 J. van Lierop, D. H. Ryan, M. E. Pumarol, and M. Roseman, J. App. Phys. **89**, 7645 (2001).
5 L. P. Le, A. Keren, G. M. Luke, B. J. Sternlieb, W. D. Wu, Y. J. Uemura, J. H. Brewer, T. M. Riseman, R. V. Upasani, L. Y. Chiang, et al., Phys. Rev. B **48**, 7284 (1993).
6 H. W. Pickering, Corrosion Sci. **23**, 1107 (1983).
7 H. Lei, Z. Song, D. Tan, X. Bao, X. Mu, B. Zong, and E. Min, Appl. Catalysis A **214**, 69 (2001).
8 J. van Lierop, H. S. Isaacs, M. Sadhur, and S. Majetich, unpublished results (2003).
9 J. van Lierop and D. Ryan, Phys. Rev. B **63**, 064406 (2001).
10 D. L. Peng, K. Sumiyama, S. Yamamuro, T. Hihara, and T. J. Konno, Phys. Stat. Sol. (a) **172**, 209 (1999).
11 S. Gangopahdyay, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde, IEEE Trans. Magn. **28**, 3174 (1992).
12 B. D. Cullity, *Introduciton to Magnetic Materials* (Addison-Wesley, Reading, MA) p. 415 (1972).
13 A. Schenck and F. N. Gygax, *Handbook of Magnetic Materials*, ed. K. H. J. Buschow (Elsevis, Amsterdam) **9**, 57 (1995).
14 R. Kubo and T. Toyabe, *Magnetic Resonance and Relaxation*, edited by R. Blinc (North-Holland, Amsterdam p. 810 (1967).
15 F. L. Pratt, T. Sasaki, N. Toyota, and K. Nagamine, Phys. Rev. Lett. **74**, 3892 (1995).