The enhancement effect in the domain and domain wall in Fe$^{57}$ nuclear magnetic resonance

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We observed both the nuclear magnetic resonance (NMR) signals from the domain and the domain wall in pure iron particles. In the multi-domain state, the total signal was divided into the signal from the domain and that from the domain wall and the enhancement factors were evaluated separately. The average enhancement factors in the domain walls and the domains were estimated to be about 136 and 34, respectively, in zero field, and remained constant in external dc field in the multi-domain state. In the single domain state, it was observed that the enhancement factor is inversely proportional to external field, and the resonance frequency decreases linearly with external field. From the comparative study between the magnetization curve and the variation curves of the domain wall signal and the resonance frequency with external field, we showed that NMR could give useful information on the magnetization process. © 1997 American Institute of Physics.

I. INTRODUCTION

It is known that the rf field experienced by a nuclear spin in the nuclear magnetic resonance (NMR) experiment of ferromagnets is enhanced due to the accompanying motion of the magnetization of electron spins. Therefore, the enhancement is related to the local electronic susceptibility and the NMR signal, which reflected local effective field, is enhanced by the same factor, and the enhancement factor in the domain walls is usually an order of magnitude larger than that in the domains.1–3 Therefore, it is believed that the NMR signals arise mainly from the nuclei in the domain walls in a multi-domain ferromagnet. Moreover, it was suggested that the domain is shielded from the applied rf field by the motion of the domain walls.4–9 However, there were reports that a mixture of signals coming from the domains and domain walls was observed. Weger observed a nonexponential fast relaxation at low rf power and an exponential slow relaxation at high rf power in the Fe$^{57}$ NMR which are believed to be the relaxations in the domain wall and domain, respectively.10 He insisted that the difference between the relaxation time in the domain wall and domain, respectively, is the main reason for a variety of the experimental values for the relaxation times. Later, Stearns reported that the Fe NMR signal disappeared at about 7 kOe dc field, at which all the domain walls were expected to be swept away.6 This implies that the signal comes mainly from the nuclei in the domain wall. Both the enhancement factor and relaxation rates depend on the location inside the domain wall, being maximum at its center, due to the variation of the angle between adjacent electron spin directions. Therefore, she insisted that in multi-domain ferromagnets the NMR signal is due mainly to the nuclei in the domain walls and the experimental value for relaxation times varies with the rf field strength because of this variation of the enhancement factor and relaxation times in the domain wall.

In our NMR experiment in iron, we could detect both the signals coming from the domain and the domain walls as Weger did. Two different relaxation processes were observed at zero field. The slower relaxation was attributed to the nuclei in the domain because it was single exponential and the ratio of the amplitudes of the fast to the slow relaxation processes decreased with increasing rf power. The most direct evidence for the fact that the slow relaxation process occurs in the domain comes from the comparison of the signal from the multi-domain state with that from the single domain state. The NMR signal was still observed at dc fields over 7.5 kOe where all the domain walls were swept away and the slower relaxation rate at zero field approached the relaxation rate of this single domain state with increasing rf field.

We could divide the mixed signal into the signal from the domain and that from the domain wall and estimated the enhancement factors separately. The ratio of the average enhancement factor in the domain wall to the enhancement factor in the domain of our sample was about 4.0. We believe that this low ratio is the main reason why a mixture of signals coming from the domain wall and domain was observed by us and Weger. No trace of the domain shielding was observed. Therefore, both points of view are correct in our opinion, that is, various relaxation times can be measured depending on the rf power level because the enhancement factors in the domain and domain wall are different or because the enhancement factor varies in the domain wall. If the ratio of the enhancement factor in the domain wall to that in the domain is low, the former is the main reason, and if the ratio is high, the latter. The absolute values of the enhancement factors were determined by comparing the rf field...
which makes the echo amplitude maximum with that of the proton NMR at the same frequency. The enhancement factors in the domain and domain wall were obtained at various external dc fields from zero to 10 kOe.

The signals obtained at short echo times and low rf power levels mainly come from the nuclei in the domain wall even when the signal is a mixture. The signal amplitude obtained in these conditions as a function of dc field approximately corresponds to the volume change of the domain wall because the enhancement factor in the domain wall remains unchanged in external dc field in the multi-domain state. The volume change of the domain wall is closely related to the magnetization process in the multi-domain state. On the other hand, the resonance frequency obtained as a function of dc field shows clearly when a single domain is formed. We compared these changes of the domain wall volume and resonance frequency with dc field to the magnetization curve to illustrate that the NMR in ferromagnets gives valuable information on the magnetization process.

II. EXPERIMENT

The sample was 99% pure natural iron powder with the size varying from 1 to 4 μm. The picture taken by scanning electron microscopy (SEM) shows that the particles are mostly spherical. The sample was annealed to remove the internal strain at 400 °C in the vacuum below 10⁻¹ Torr for 4 h. The spin echo amplitudes following a pair of pulses \( \Delta t - t = 2 \Delta t \) were measured at room temperature as a function of the time interval \( t \) between the pulses, rf field and dc field. The linewidth obtained by the Fourier transform of the spin echo was 50 kHz. The pulse width \( \Delta t \) was 1.5 μs, which was short enough to excite the whole range of the spectrum. The resonance frequency was measured at various dc fields from zero up to 10 kOe. The magnetization curve was measured by a vibrating sample magnetometer (VSM).

It is necessary to measure the rf field strength to obtain the enhancement factors. Since it is difficult to accurately measure the absolute rf field inside the sample coil, it was estimated by comparison with that of the proton NMR. This was done by measuring the voltage developed across a single turn of wire fitting closely around the sample, which is proportional to the field generated by the rf coil. This voltage was compared with that of the proton NMR when the signal amplitude was maximum. This gives the enhancement factor of our sample because the enhancement factor is inversely proportional to this voltage, and the rf field when the proton NMR signal is maximum is theoretically predictable. The enhancement factor estimated in this way gives the enhanced rf field level which the nuclei see over that seen by the electrons.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. The NMR frequency versus external dc field

Figure 1 shows the resonance frequency measured at various dc fields up to 10 kOe at room temperature. The NMR signal was observed at an echo time of 100 μs which is much shorter than the average spin-spin relaxation time in the domain wall. Therefore, the observed signal mainly comes from the nuclei in the domain wall. At zero field, the NMR frequency is proportional to the hyperfine field which is estimated from Fig. 1 to be 330.2 kOe. The resonance frequency remains unchanged up to 6 kOe, and above that decreases slowly. At non-zero external fields, the field experienced by a nuclear spin is the vector sum of the hyperfine field and external field. In the domain walls, these two fields are not generally parallel and the amplitude of the total field changes negligibly with external field because usually external fields are much weaker than the hyperfine field. Therefore, the resonance frequency is expected to be independent of external field as far as the signal from the domain walls dominates. However, if two fields are parallel as in the single domain state, the NMR frequency is proportional to the external field. In this case, the resonance frequency \( \omega \) is given by

\[
\omega = \gamma_n (H_n + H_0 - H_d),
\]

where \( \gamma_n \) is the gyromagnetic ratio of iron nucleus and \( H_n, H_0, \) and \( H_d \) are the hyperfine, external and demagnetization fields, respectively. The resonance frequency in Fig. 1 decreases linearly with external field above 7.5 kOe indicating that a single domain was formed, and actually the data fits well to Eq. (1) with the correct tangent \( \gamma_n \) (solid line). Since the negative tangent implies that the total magnetic field decreases with increasing external field, the hyperfine and external fields are anti-parallel, that is, the hyperfine field is opposite to the magnetization by the electron spins and therefore the sign of the hyperfine constant in iron is negative.

The sign of the hyperfine field in iron has been known to be negative by a Mössbauer experiment, but never confirmed by NMR as far as we know.

The macroscopic difference between single domain and multi-domain samples in zero field is the magnetization. Therefore, the difference between the resonance frequencies of single domain and multi-domain particles at zero field corresponds to the demagnetization field. The resonance fre-
quency of the single domain state at zero field was obtained by extrapolating the linear fit of the data above 7.5 kOe to Eq. (1). The demagnetization field estimated in this way was 7.3±0.7 kOe. This is in good agreement with the theoretical value 7.2 kOe which is the saturation magnetization 21.5 kG of iron multiplied by the demagnetization factor 1/3 for a spherical sample.

B. The signals from the domain and domain wall

Since the enhancement factors in the domain and domain wall are different, the flip angles of nuclear spins are also different for a given rf power. When the rf pulse is not strong enough to make the average flip angle of the nuclear spins in the domain walls 90°, the signal coming from the domain wall is dominant. If the rf pulse power is increased higher than the average 90° pulse power for the nuclear spins in the domain wall, the distribution of the flip angles in the domain walls tends to cancel out the resulting echo amplitude, while the signal from the domain keeps increasing until the flip angle of the nuclei in the domain reaches 90°. In this range, therefore, the contribution of nuclear spins in the domain to the total signal increases with the rf power. This is shown in Fig. 2 where the relative spin echo amplitude is plotted as a function of external dc field at various rf powers and echo times. At low rf field (H_1=0.6 in arbitrary unit), the signal decreases with increasing dc field until it almost disappears over 7.5 kOe where a single domain is formed. Therefore, the signal at this field is mostly due to the nuclei in the domain wall. The signal amplitude is proportional to both the volume of the domain walls and the average enhancement factor in the domain walls. Since the enhancement factor in the domain walls is almost independent of dc field as discussed in the next section, the signal at H_1=0.6 approximately represents the volume change of the domain wall with external dc field. The absolute signal amplitude decreases with dc field at any rf field, but the relative signal amplitude at dc fields above 7.5 kOe increases with the rf field, which means that the contribution of the signal from the domains increases. The data for H_1=7.5 and an echo time of 3 ms especially remains almost constant in the multi-domain state. It is obvious that the contribution of the nuclei in the domain wall to the total signal is almost negligible in this case. The signal decrease in the single domain state is due to the dependence of the enhancement factor in the domain on dc field as discussed in the next section.

Several authors mentioned the shielding of the domain bulk from the applied rf power by the motion of the domain walls as one of the reasons for the fact that only the domain wall signal is observed, referring to Portis and Gossard’s original work. If the domain is shielded, the domain signal is expected to increase as the domain walls are swept away. However, the data in Fig. 2 show no trace of shielding. The almost pure domain signal (H_1=7.5 and an echo time of 3 ms) remains constant in the multi-domain state and smoothly connects to that in the single domain state.

Figure 2 also shows that the ratio of the signal coming from the domain to that from the domain wall depends on the echo time. At low rf power levels and short echo times, the domain wall signal is dominant while at high rf power levels and long echo times, the domain signal is dominant. This implies that the enhancement factor is smaller and spin-spin relaxation time is longer in the domain than in the domain wall. The echo amplitudes are plotted as a function of the echo time at various rf power levels in zero field in Fig. 3. At low rf power levels, the relaxation curve is not single exponential and has at least two components. The slower relaxation process fits well to a single exponential (solid lines), of which the relative amplitude increases with increasing rf power. The relaxation time of the slower process also increases with rf power and approaches that of the single exponential decay obtained in the single domain state at 8
Therefore, this slower relaxation process is associated with the domain.

C. The enhancement factors

One of the ways to obtain the information on the enhancement factors is to plot the spin echo amplitude as a function of rf power as in Fig. 4. For any echo time, the amplitudes decrease monotonically after the maximum. As the echo time increases, the peak height of the echo decreases and the corresponding peak rf field increases because the signal coming from the domain becomes progressively dominant with the increasing echo time as seen in the previous figures, Figs. 2 and 3. Since a nuclear flip angle is proportional to the product of the enhancement factor and rf field, the peak field is the measure of the average enhancement factor of the whole sample. The relation between the peak rf field and the echo time is shown in Fig. 5. The peak field increases fast initially, but approaches a constant value with the echo time. This means that the NMR signal coming from the domain walls is fully relaxed and the signal is only due to the nuclei in the domains when the echo time is long enough, say 30 ms. The asymptotic peak field in the infinite echo time limit corresponds to the 90° rf pulse field for the nuclei in the domain. Therefore, the enhancement factor in the domain wall is inversely proportional to this asymptotic peak rf field. By comparison of this peak rf field to that of the proton NMR, the enhancement factor in the domain was estimated to be 34.

Since the echo signal at an echo time of 30 ms is almost purely due to the nuclei in the domain, it can be used to divide a mixed signal at a short echo time into the signals from the domain and domain wall. In Fig. 4, the dashed line is the data for an echo time of 30 ms amplified to fit to the data for an echo time of 100 μs. The good match between them over \( H_1 = 10 \) confirms that the domain signal is dominant at high rf power levels. The difference between them (solid line) at low rf power should come from the domain wall. The peak rf field of the domain wall signal is about four times smaller than that of the domain, meaning that the average enhancement factor in the domain walls is about 136. The average enhancement factor in the domain wall at room temperature has been reported in a wide range from 100 to 1800\(^1,6,7,14\) depending on the sample properties such as purity and internal strain. This small difference between the enhancement factors in the domain and domain wall is the main reason why a mixed signal is observed in our sample.

The monotonic, instead of oscillatory, decay of the echo amplitude after the maximum was well explained by the drumhead model of the domain wall where the enhancement factor depends not only on the position across the wall, but also the radius in the wall plane.\(^6\) When the enhancement factor in the domain wall center is \( e_0 \), the enhancement factor at the distance \( x \) across the domain wall from its center has the distribution of the form \( e_0 \text{sech} x \). If the domain walls are assumed as circular membranes of finite radii, like drumheads, the domain wall signal following a pair of pulses \( \Delta \tau - t - 2\Delta \tau \) is given by

\[
S = \frac{1}{2} m_0 e_0 \int_0^\infty \int_0^1 \sin^3(\alpha_0 z \cdot \text{sech} x) z \times \text{sech} x \ln^2(1/z) dz \, dx,
\]

where \( m_0 \) is the nuclear magnetization and \( z \) is the radius. The flip angle of a nuclear spin \( \alpha_0 \) is given by \( e_0 \gamma_0 H_1 \Delta \tau \) where \( H_1 \) is the rf field. The maximum enhancement factor in the domain wall center estimated by fitting this model to the domain wall signal obtained above is 580.

In Fig. 6, the average enhancement factor in the domain wall and the enhancement factor in the domain are plotted at various external dc fields from zero to 10 kOe. The enhancement factors in the multi-domain state were obtained by the
analyses described above in each field. In the single domain state, of course, these analyses are not necessary and the enhancement factor is calculated simply from the peak rf field of the experimentally observed signal. In the multi-domain state, the average enhancement factor in the domain wall \(H\) is almost independent of external dc field in consistence with the previous report.\(^6\) The enhancement factor in the domain \(H\) is also independent of dc field in the multi-domain state. However, it is inversely proportional to external dc field in the single domain state. A simple model on the enhancement effect predicts the enhancement factor in a domain approximately as\(^3\)

\[
\epsilon = \frac{H_a}{H_0 + H_A},
\]

where \(H_A\) is the anisotropy field in a sample. Equation (3) qualitatively explains the dependence of the enhancement factor on external dc field above 7.5 kOe. This field dependence of the enhancement factor in the single domain state is also reflected in the echo signal decay (Fig. 2). However, the success of this simple model is limited to the qualitative prediction of the inverse proportionality of the enhancement factor to external field and the application of this simple model to our experimental data produces unrealistic hyperfine and anisotropy fields.

**D. The magnetization process**

The NMR echo amplitude and resonance frequency can give valuable information on the magnetization process. In general, the magnetization process in a multi-domain particle is understood as the following.\(^13\) At zero field, a multi-domain particle is in the demagnetized state on the whole because the magnetic moment of each domain randomly directs to easy axes. At a weak magnetic field, the domain walls move to increase the volume of the domains which are aligned favorably with respect to the external field. At an increased field, the magnetization of the unfavorably aligned domains rotate to the easy axis nearest to the external field. In this process, the volume of the domain walls decreases fast because of the merging of the domains. At a much stronger field, all the domains align to the external field direction to form a single domain where the technical saturation is accomplished.

In Fig. 7, parts of Fig. 1 and Fig. 2 and the magnetization curve of our sample are plotted together to understand the magnetization process synthetically. The spin echo amplitude at \(H=0.6\) approximately corresponds to the volume change of the domain wall with external field as discussed above. The domain wall volume starts a fast decay at about 3 kOe. Up to this field, the domain wall motion is the main magnetization process. The domain wall volume decreases a little bit, but the magnetization almost reaches its saturation. Above 3 kOe, the domain rotation becomes dominant and the domain wall volume decreases fast, while the magnetization increases a little bit. The resonance frequency change...
shows that the domain walls almost disappear above 6 kOe and the sample becomes a complete single domain where all the magnetic moment of the electron spins align to the external field direction at 7.5 kOe.