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External Field Dependence of Fe^{57} NMR in Pure Iron

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The NMR spin echo in pure iron was measured as a function of external magnetic field up to 10 kgauss at room temperature. We observed the signal coming from a single domain formed over 7.5 kgauss which has not been detected in previous works. The resonance frequency shift with external field confirmed that the hyperfine field in iron is −330.2 kgauss. From the comparison of the magnetization curve with the domain wall signal and the resonance frequency in external field, we showed that NMR could give the useful qualitative information on the magnetization process. The extent of the internal strain removed by annealing, which can be hardly seen in hysteresis curves, was clearly shown up in the NMR line-width.

1. Introduction

The nuclear magnetic resonance (NMR) is known as a useful tool to study ferromagnetic and antiferromagnetic materials. The NMR line-width, resonance frequency and the dependence of signal heights and relaxation times on external field could give information about macroscopic and microscopic properties of magnetic materials such as the magnetization process, domain wall motion, demagnetization field, easy axis, spin waves, magnetic susceptibility and hyperfine interaction. The NMR in Co and Fe, which is a typical ferromagnetic transition metal, was first reported in a cobalt by Gossard, Portis and Sandle [1] and in a natural iron by Winter and Robert [2].

The NMR signal in ferromagnetic materials is $10^2 - 10^4$ times greater than that in non-magnetic materials by the enhancement effect. Because this enhancement effect is usually much larger in domain walls than in domains, the signal comes mainly from the nuclei in domain walls [1-6]. It is often necessary to measure the NMR signal of domains, because its relaxation times, resonance frequency, line width, etc. are different from those of domain walls in addition to the enhancement factor. One method to observe the NMR signal of domains is to sweep away all domain walls by a strong external field, but there has been no report about the observation of NMR signal of domains in this way as far as we know.

The NMR experiments described in this work were done in the external field from 0 to 10 kgauss, and we observed not only the signal coming from domain walls but also that from a single domain after all domain walls were swept away. From the NMR signal of domain walls changing with external field, we could get information on the domain wall motion and domain rotation in the magnetization process of ferromagnetic materials. From the NMR signal of domains, the magnetic field where a complete single domain is formed was estimated. The sign of the hyperfine field was decided from the dependence of the resonance frequency on external field in a single domain state. The NMR and Mössbauer experiments are known as the main tools to study the hyperfine field in magnetic materials [3, 4, 7, 8]. The absolute value of the hyperfine field can be estimated from the NMR frequency at zero field and the sign can be decided from the dependence of the resonance frequency on external field. However, the resonance frequency is almost independent of external field in a multi-domain state, and therefore, the sign can be decided after a single domain is formed by external field. Also, by comparing the NMR line-width of the natural sample with that of the annealed one, the extent of the

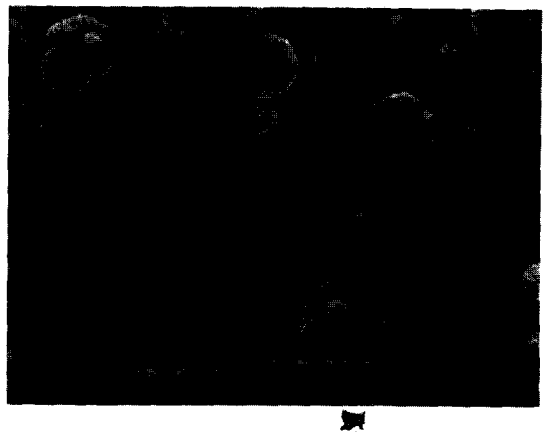

Fig. 1. The picture of the spherical iron powder taken by SEM. The size is in the range of $1-4$ μm.

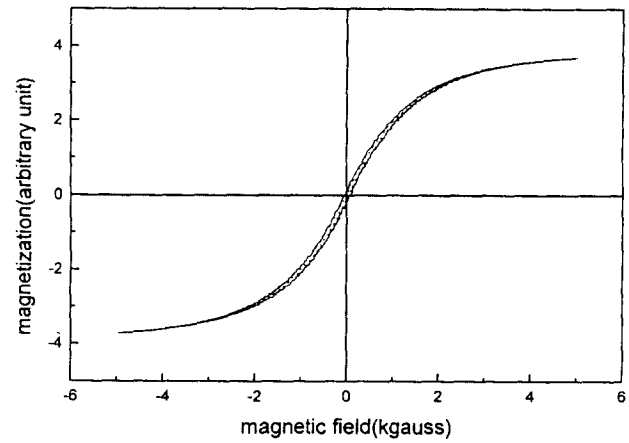

Fig. 2. The hysteresis curves of the annealed (solid line) and natural iron (dashed line).

internal strain removed by annealing was quantitatively estimated, which wasn't clear in the hysteresis curves.

2. Experiment

The sample was 99 % pure natural iron powders with the size varying from $1-4$ μm. The picture taken by a scanning electron microscope (SEM) shows that the powders are mostly spherical (Fig. 1). The sample was annealed at 400 ℃ in the vacuum below 10^{-1} torr for 4 hours. The annealed samples were used in all NMR experiments except in the line-width measurement which was to show the effect of annealing. We measured the spin echoes at echo times 140 μsec or 3 msec following a pair of pulses ($\Delta\tau - t - 2\Delta\tau -$, $\Delta\tau$; pulse width) at room temperature. The resonance frequency and echo amplitude were measured as a function of external field with fixed pulse width 1.5 μsec. The external field was varied from zero up to 10 kgauss. The hysteresis curve was measured by a vibrating sample magnetometer (VSM).

3. Results and Discussion

1) The annealing effect shown in the line-width change

Fig. 2 is the hysteresis curves of the natural and annealed iron measured at room temperature. The coercive fields of both samples were about 50 gauss as seen in Fig. 2, so the samples are close to a soft magnetic material. Though the difference between the natural and annealed iron is negligible in these hysteresis curves, it becomes clear in the NMR spectrum of Fig. 3. As seen in this NMR spectrum measured without external field, the line-width was reduced from about 160 kHz in the natural iron to about 50 kHz in the annealed iron. The NMR line-width of an iron was observed over the wide range from about 8 kHz to several hundred kHz [2, 3, 5, 6, 9-12]. The NMR spectrum in ferromagnetic materials is inhomogeneously broadened by the inhomogeneous spin waves in the domain walls intrinsically [13].

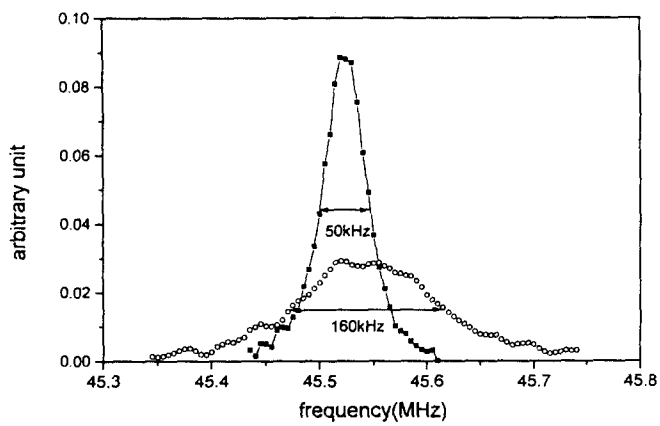

Fig. 3. The NMR spectrum of the annealed (solid square) and natural (open circle) iron at room temperature.

That inhomogeneous broadening was estimated about 13-15 kHz in iron [10, 11]. The extra broadening of the line-width is due to impurity and internal strain [9, 10, 14]. The annealing removes internal strain of a sample [10]. Because internal strain can be thought as a source of an anisotropy field in addition to that by the crystallographic structure, the line-width narrowing in the annealed iron is due to the decreased internal strain that has existed in the natural iron. The line-width reduced by annealing is 110 kHz which corresponds to the inhomogeneous field of 0.8 kgauss. The reduced anisotropy energy due to this eliminated internal strain is 1.4×10^6 erg/cm^3 in iron. Because the line-width is broader than the minimum values of previous results and the value estimated from the inhomogeneous broadening by spin waves in domain walls, the internal strain seems to be partially removed by annealing.

2) The resonance frequency shift vs. external dc field

Fig. 4 shows the resonance frequency changing as a function of external field up to 10 kgauss in the annealed iron at room temperature. The resonance frequency remains unchanged up to

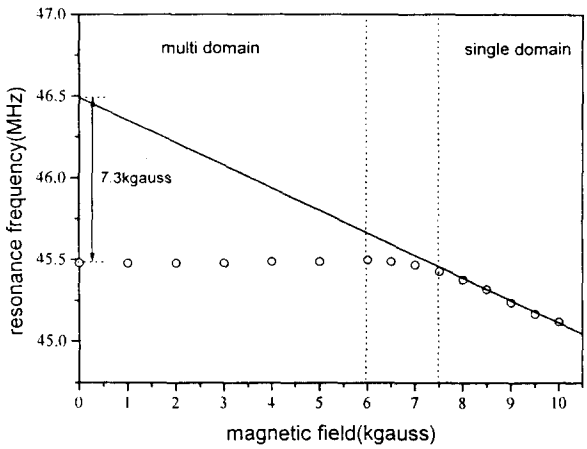

Fig. 4. The resonance frequency vs. external field.

6 kgauss over which it starts to decrease slowly. Over 7.5 kgauss, the resonance frequency decreases linearly with external field. The resonance frequency change with external field is closely related to the magnetization process. In general, the magnetization process in a multi-domain particle is understood as the following [15]. At zero field, a multi domain particle is in a demagnetized state on the whole because the magnetic moment of each domain randomly directs to easy axes. At a weak magnetic field, domain walls move to increase the volume of domains which are aligned favourably with respect to the external field. At an increased field, the magnetization of the unfavourably aligned domains rotates to easy axis nearest to the external field. In this process, the volume of domain walls decreases fast because of the merging of domains. At a much stronger field, all domains align to the external field direction to form a single domain where the 'technical saturation' is accomplished, so to speak.

The magnetic field that is experienced by a nuclear spin is the sum of the hyperfine field and an external field. At zero field, the NMR frequency is proportional to the hyperfine field which is parallel or anti-parallel with the external field. The hyperfine

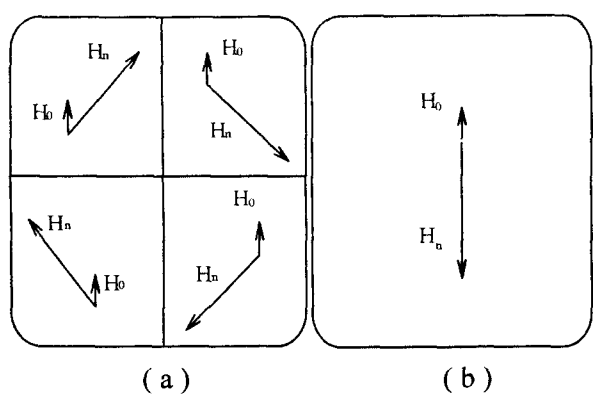

Fig. 5. The hyperfine field H_n and an external field H_0 in (a) multi-domains and in (b) a single domain.

field that is estimated from Fig. 4 is 330.2 kgauss at room temperature. As seen from Fig. 5a, two magnetic fields, the hyperfine and external, are not generally parallel even in domains of the multi-domain state and there is little dependence of the resonance frequency on the external field because usually the external field is much smaller than the hyperfine field. The multi-domain state continues to about 6 kgauss because negligible change in the NMR frequency is observed up to this field. For the hyperfine field H_n and the external field H_0, the NMR frequency change is proportional to $(H_0/H_n)^2$ approximately, so in an external field of 6 kgauss the frequency shift is expected to be only about 1/3000 in iron. However, if two magnetic fields are parallel as in a single domain Fig. 5b, the NMR frequency is proportional to the external field. In this case, the resonance frequency w is given by

$$w = \gamma_n (H_n + H_0 - H_d), \tag{1}$$

where γ_n is the gyromagnetic ratio of iron nuclear and H_d is the demagnetization field. The resonance frequency in Fig. 4 decreases linearly with the external field above 7.5 kgauss indicating that a single domain was formed, and actually data fits well to eq. (1). with the correct tangent γ_n. The negative tangent implies that the total magnetic field, which is a vector sum of the hyperfine field and the external field, decreases with the increasing external field. This means that the external field and the hyperfine field are anti-parallel, that is, the direction of the hyperfine field is opposite to the magnetization by electron spins and therefore the sign of the hyperfine field in iron is negative. The sign of the hyperfine field in iron has been known as negative by Mössbauer experiment [7], but never confirmed by NMR before.

The macroscopic difference between a single domain and a multi-domain samples in zero field is the magnetization. Therefore, the difference between the resonance frequencies of a single domain and multi-domain particle at zero field corresponds to the demagnetization field. The resonance frequency of a single domain at zero field was obtained by extrapolating the linear fitting (solid line) of the data above 7.5 kgauss to eq. (1). The demagnetization field estimated in this way was 7.3 ± 0.7 kgauss. This is in good agreement with the theoretical value 7.2 kgauss that is the saturation magnetization 1710 gauss [15] of iron multiplied by the demagnetization factor $4\pi/3$ for a spherical sample.

3) The spin echo amplitude vs. external dc field

It is known that an r.f field, which is experienced by a nuclear spin, is enhanced due to the motion of the magnetization of electron spins by the applied r.f field. The NMR signal is enhanced by the same factor, and the enhancement factor in domain walls is generally much larger than that in domains as mentioned above. When both the nuclei in domain walls and in domains contribute to the NMR signal, the signal is given by

$$S \propto \{ \eta_{dw} V_{dw} \sin(\eta_{dw}(x)\gamma_n H_1 \Delta\tau) + \eta_d V_d \sin(\eta_d(x)\gamma_n H_1 \Delta\tau)\}, \quad (2)$$

where $\eta_{dw}(x)$ is the enhancement factor in a position x within domain walls, η_d is the enhancement factor in domains, and V_{dw} and V_d are the volume of domain walls and domains, respectively. The distribution of the enhancement factor in domain walls is due to the variation of the angle between adjacent electron spin directions in domain walls [6]. The angle of the sine function is the flip angle of a nuclear spin that is dependent on enhancement factor. When the average flip angle in domain walls is close to 90°, the signal coming from domain walls is dominant because $\eta_{dw} \gg \eta_d$. When the r.f pulse is large enough to make the flip angle 90° in domains, the distribution of the flip angle in the domain walls tends to cancel out the resulting echo signal and therefore the contribution of the signal coming from domains increases. The absolute size of the signal decreases due to the small enhancement factor of domains. The signal coming from domains was not observed in previous works, but we could observe the spin echo of domains by increasing the r.f pulse power.

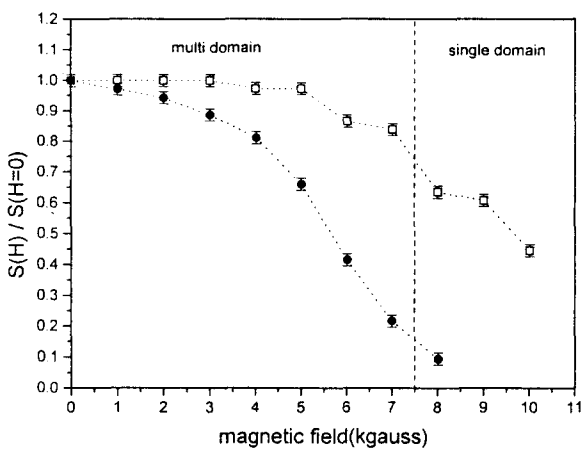

Fig. 6. The echo amplitude vs. external field. Echo times are 140 μsec and 3 msec for low H_1 (solid circle) and high H_1 (open square), respectively.

Fig. 6 is the relative change of the spin echo in iron plotted as a function of external field up to 10 kgauss at room temperature. Since a single domain is formed above 7.5 kgauss, as seen in Fig. 4, only the domains could contribute to the signal in that region and both the domains and domain walls contribute below 7.5 kgauss. In Fig. 6, the signal decreases with increasing external field, but still remains large above 7.5 kgauss when the r.f field is high, which means the contribution of the signal from domains is not negligible at zero field. However, when the r.f field is low, the signal disappears as the sample becomes a single domain, meaning that the contribution of the signal from domain walls is dominant at zero field. The signal coming from domain walls is proportional to the volume of the domain walls and the average enhancement factor in domain walls. Since the enhancement factor in domain walls is almost independent of external field [6], the signal at low r.f field in Fig. 6 corresponds to the change of the domain wall volume with the external field. The domain wall volume decreases fast above 3 kgauss, indicating that the domain rotation becomes dominant.

4) Summary of the magnetization process

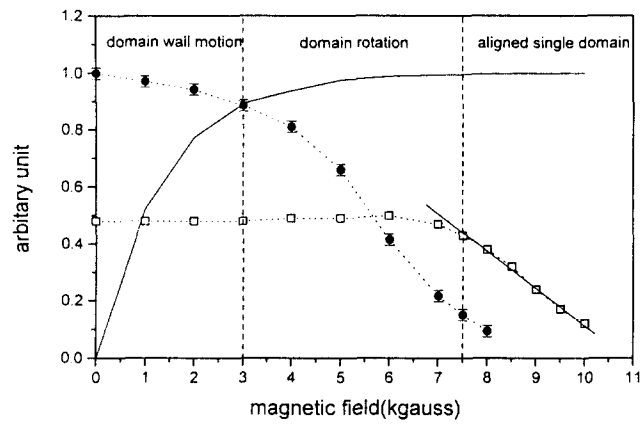

Fig. 7. The magnetization (solid line), domain wall volume (solid circle), and the resonance frequency (open square) vs. external field.

In Fig. 7, parts of Fig. 2, 4 and 6 are plotted together to understand the magnetization process synthetically. The domain wall volume starts a fast decay above about 3 kgauss. 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. At above 3 kgauss, the domain rotation becomes dominant and the domain wall decreases fast. During that period, the number of domains decreases fast and the magnetization increases a little bit. The domain walls almost disappear above 6 kgauss as seen in the resonance frequency change 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 kgauss.

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