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# DYNAMICAL MAGNETIC PROPERTIES OF IRON-NITRIDE MAGNETIC FLUIDS

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*Abstract-* Ac susceptibility of iron-nitride magnetic fluids with various particle number densities was measured. The relaxation time increases rapidly as the temperature decreases or the inter-particle interaction increases. The analysis of the data suggests that the activation energy is proportional to $(k_B T/J_{typ})^{\alpha}$ with $\alpha \sim -0.24$ in the lower temperature range in which the thermal energy is comparable to the magnetic dipole interaction.

## I. INTRODUCTION

In recent years, the magnetic properties of frozen magnetic fluids have been intensively investigated because of the general interest in random magnetic material [1,2].

In an isolated single domain particle, the magnetic moment relaxes by overriding the anisotropy energy barrier $K_u V$. The relaxation time $\tau$ obeys the following Arrhenius law [3]

$$\tau = \tau_0 \exp(E_a/k_B T), \tag{1}$$

$$E_a = K_u V, \tag{2}$$

where $\tau_0$ is a time factor, $E_a$ the activation energy, $K_u$ the anisotropy constant, $V$ the volume of the particle, $k_B$ the Boltzmann constant, $T$ the absolute temperature. Recently Dickson et al suggested that the appropriate value of $\tau_0$ lies in the range $10^{-12}$ to $10^{-13}$ s [4], though the value of $10^{-9}$ s has been commonly used [3].

In magnetic fluids, stable colloidal suspensions of single domain particles, the relaxation process is affected by magnetic dipole interaction; this interaction energy between the moments $\vec{\mu}_j$ of the particle $j$ and that of the particle $i$ is described as

$$E_{ij} = -\vec{\mu}_i \cdot \vec{H}_{ji} = \vec{\mu}_i \cdot [(\vec{\mu}_j - 3\hat{r}_{ji}(\vec{\mu}_j \cdot \hat{r}_{ji}))/r_{ji}^3], \tag{3}$$

where $\hat{r}_{ji}$ is a unit vector from the particle j to i, $r_{ji}$ the distance between particle j and i. Thus the interaction is expected to be proportional to the particle number density $n$ because of the dependence on $1/r_{ji}^3$ as shown in eq. (3).

In this study, to clarify the effect of magnetic inter-particle interaction in frozen magnetic fluids, ac susceptibility $\chi = \chi' + i\chi''$ of iron-nitride magnetic fluids with various particle number densities was measured. Iron-nitride magnetic fluids are suitable for this purpose, because they are uniform in size (see Fig. 1) and have fairly strong interaction expected from the large magnetization compared with conventional oxide magnetic fluids [5].

## II. EXPERIMENTAL

Iron-nitride magnetic fluids are prepared by a method of vapor-liquid chemical reaction between iron carbonyl and ammonia [5]. The carrier liquid of the magnetic fluids is kerosine: its freezing temperature is about 200K. Table I summarizes the particle number density of the samples. Sample A1 is the as-prepared iron-nitride magnetic fluids and the others are its dilution. The analysis of the magnetization process of sample A1 shows that the mean magnetic moment $\bar{\mu}$ is $1.8 \times 10^{-16}$ emu, the magnetic mean diameter of the particles is 5.7nm, and the particle number density $n$ is $1.6 \times 10^{17}/\mathrm{cm}^3$ [5]. The particle size distribution of sample A1 decided from the electron micrograph is shown in Fig. 1 [5]. These characteristic parameters are invariant with diluting the sample except the particle number density $n$.

Ac susceptibility was measured by a conventional mutual-inductance method at various temperatures from 4.2 to 300K after the zero field cooling process. In low frequency range from 5Hz

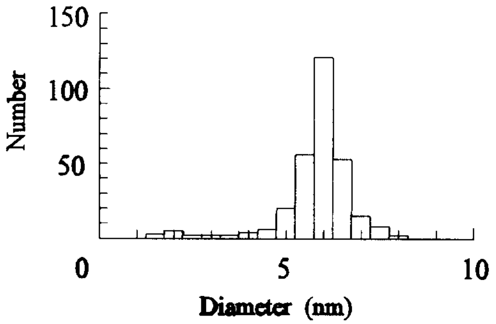

**Fig. 1.** The particle size distribution on the electron micrograph of sample A1.

**Table I.** The particle number density of the samples. The value of sample A 1 is estimated from its magnetization process [5] and those of the other samples are calculated from the dilution ratio.

| Sample | A 1 | A 2 | A 3 | A 4 | A 5 | A 6 |
|---|---|---|---|---|---|---|
| $n$ (/cm$^3$) | $1.6\times10^{17}$ | $7.7\times10^{16}$ | $3.8\times10^{16}$ | $2.0\times10^{16}$ | $4.8\times10^{15}$ | $1.5\times10^{15}$ |

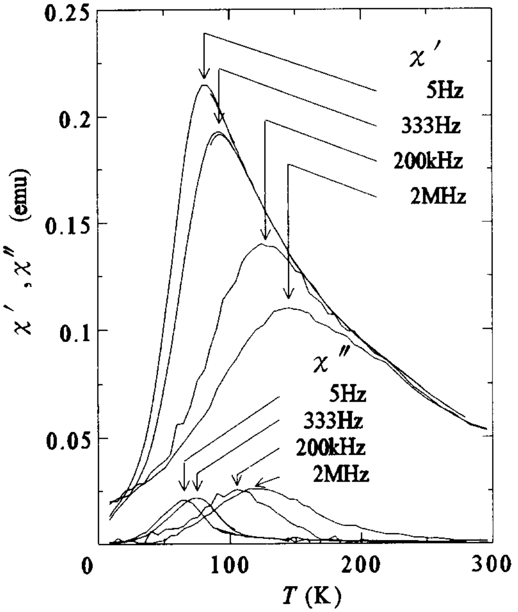

**Fig. 2.** The temperature dependence of $\chi'$ and $\chi''$ at selected measuring frequency for sample A1.

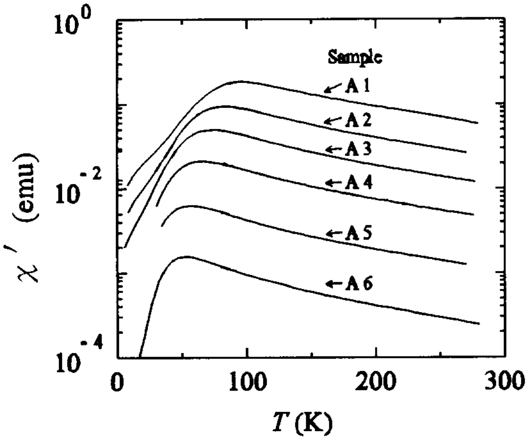

**Fig. 3.** The temperature dependence of $\chi'$ at the measuring frequency 1kHz for various samples

to 1kHz, Lake Shore model 7000 measurement system was used, where the sample was contained in the spherical cell. In high frequency range from 30kHz to 2.5MHz, Iwatsuu SY-8232 measurement system was used, where the sample cell shape was toroidal.

## III. RESULTS

Figure 2 shows the temperature dependence of $\chi'$ and $\chi''$ for sample A1 at the ac magnetic field amplitude of 1 Oe at various frequencies, where the data are corrected for the demagnetization effects. As the temperature decreases from the room temperature, the in-phase component $\chi'$ increases and shows a maximum at a certain temperature $T_m'$. The experiment at the frequency 333Hz shows that $T_m'$ has little dependence on the ac magnetic field amplitude in the field amplitude range from $10^{-2}$ to 10Oe ($\Delta T_m' \lesssim 1$K). The out-of-phase component $\chi''$ also increases with decreasing temperature and has a maximum at a certain temperature $T_m''$, which is slightly lower than $T_m'$. Both $T_m'$ and $T_m''$ increase as the frequency increases. In the temperature range $T \lesssim T_m'$, $\chi'$ decreases as the frequency increases. In the temperature range $T \gg T_m'$, $\chi'$ is independent of the frequency. Both the temperature dependence of $\chi'$ and that of $\chi''$ seem to have no anomaly at the freezing temperature of the carrier liquid (~200K). The properties mentioned in this section are common to all of the samples studied here.

Figure 3 shows the temperature dependence of $\chi'$ at the frequency 1kHz for various samples. The magnitude of $\chi'$ and $\chi''$ is almost proportional to their particle number density. Both $T_m'$ and $T_m''$ increase as the particle number density increases.

## IV. DISCUSSION

In the temperature range $T \gg T_m'$, $\chi'$ is independent of the frequency. This result indicates that $\chi'$ is equal to the equilibrium susceptibility and that the relaxation time $\tau$ is much shorter than the characteristic time of the observations $1/(2\pi f)$. While in the temperature range $T \lesssim T_m'$, $\chi'$ decreases as the frequency increases. This result indicates that $\tau$ is comparable to $1/(2\pi f)$. Thus we assume the following equation:

$$\tau(T_m')=\frac{1}{2\pi f}. \qquad (4)$$

The temperature dependence of the relaxation time for various samples calculated by the equation (4) is presented in Fig. 4. It is obvious that the relaxation time increases rapidly as the temperature decreases and also increases as the particle number density increases (□→●). These results clearly indicate that the relaxation time depends not only on the temperature but also on the magnetic dipole interaction.

In Fig 4, log $\tau$ for all of the samples appears to have the quasi-linear dependence on $1/T$ with the gradient which increases as the particle number density increases. These results suggest that the relaxation process in magnetic fluids bases on a thermal activation process and that the activation energy $E_a$ increases as the magnetic dipole interaction increases.

The magnetic dipole interaction energy at the distance of closest approach is on the order of $\bar{\mu}^2/r^3$ ($\sim\bar{\mu}^2 n$) from eq.(3), where r is the distance between the nearest neighbor particles. Thus this value $\bar{\mu}^2 n$ can be taken as a typical interaction energy $J_{typ}$:

$$J_{typ}=\bar{\mu}^2 n. \qquad (5)$$

The estimated value of $J_{typ}/k_B$ are various from 38K of sample A1 to 0.35K of the most diluted sample A6. This result shows that the interaction energy can not be neglected for the thermal energy $k_BT$ in the temperature range of the observations. Thus we consider that the increase of $E_a$ is due to the variation of the ratio $k_BT/J_{typ}$. Figure 5 shows the dependence on the ratio $k_BT/J_{typ}$ of $E_a$ for various samples, where $E_a$ is calculated by using the eq. (1) and $\tau_0=10^{-12}$s. It is evident that $E_a$ increases rapidly in the lower temperature range in which the thermal energy is comparable to the magnetic dipole interaction energy. The inset shows that all of the data for various samples lie on one straight line expressed as the following equation in the range $k_BT/J_{typ}\leq 15$ (see the solid line in the inset).

$$E_a=2300\times(T/J_{typ})^{-0.24}, \qquad (6)$$

This characteristic is similar to that of the model proposed for spin glass by Binder et al [6], though in this model the dominant component of the activation energy $E_a$ is the magnetic interaction energy. On the other hand, in the range $k_BT/J_{typ}\gg 10$ the activation energy seems to approach a value around $1\times10^3$K as $k_BT/J_{typ}$ increases (see the broken line in Fig. 5).This value is considered

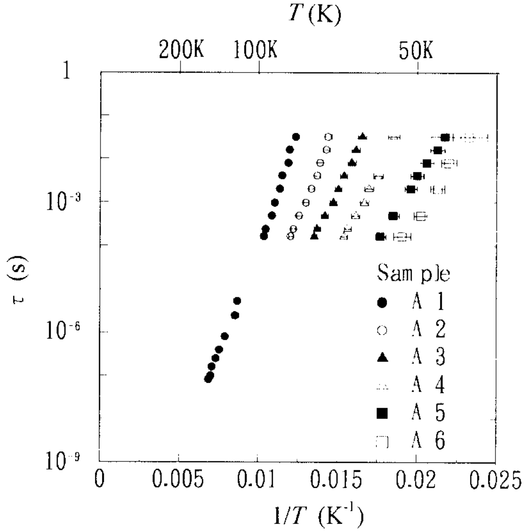

**Fig.4.** The temperature dependence of the relaxation time in the plot of log $\tau$ versus $1/T$ for various samples.

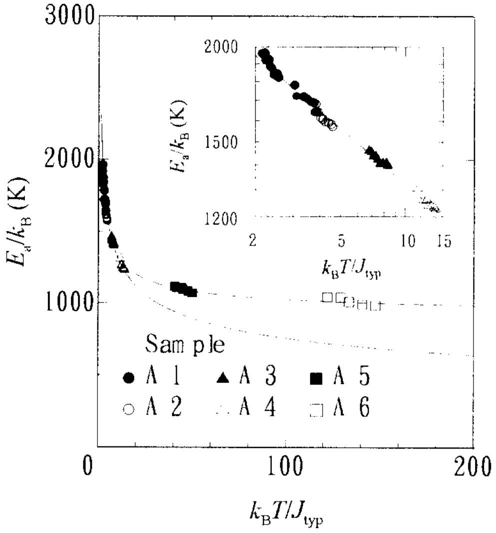

**Fig.5.** $E_a$ versus $k_BT/J_{typ}$ for various sample. The inset shows the details in low value range of $k_BT/J_{typ}$ in log-log plot. The solid line is given by eq.(5). The broken line is guide for eye.

to be the anisotropic energy $K_uV$ for the isolated particles. The value lead to a reasonable value of the anisotropic constant of iron-nitride $K_u \approx 1 \times 10^6$erg/cm$^3$. This characteristics hold while $\tau_0$ is in the range $10^{-12}$ to $10^{-13}$ s suggested by Dickson et al [4]. Using the value $\tau_0 = 10^{-9}$s, the data for various samples can not be scaled.

## V. SUMMARY

The relaxation time of iron-nitride magnetic fluids increases as the magnetic inter-particle interaction increases and also increases as the particle number density increases. The temperature dependence of the relaxation time suggests that a thermal activation process dominantes the relaxation process. The activation energy appears to be proportional to $(k_BT/J_{typ})^\alpha$ with $\alpha \sim -0.24$ in the lower temperature range, in which the thermal energy is comparable to the magnetic dipole interaction energy. On the other hand, the samples with weak magnetic interaction seem to have the activation energy $E_a$ which approaches the anisotropy energy of isolated particles $K_uV \approx 1 \times 10^3$ K·$k_B$ as $k_BT/J_{typ}$ increases.

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