Magnetic Relaxations of Antiferromagnetic Nanoparticles in Magnetic Fields

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We reexamine anomalous magnetic relaxations of ferritin in magnetic fields, the presence of which has been regarded as evidence suggesting the existence of thermally assisted macroscopic quantum tunneling in antiferromagnetic nanoparticles. In the present study, relaxation curves of ferritin are examined using an approach that is free from assumptions regarding distributions of various parameters of polydispersive particles. The results are not anomalous. In other words, the relaxation is accelerated by the field, as expected for classical superparamagnetic fluctuations.

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Recently, a rich potential for nanomagnets in quantum computing hardware [1,2] has been proposed based on intensive studies carried out in the 1990s [3–5]. In such studies, pure and thermally assisted macroscopic quantum tunneling was investigated with regard to the dynamics of magnetic moments of various nanomagnets: molecular magnets ($\sim 10^1 \mu_B$) [3], antiferromagnetic nanoparticles ($\sim 10^2 \mu_B$) [4], and ferromagnetic nanoparticles ($> 10^3 \mu_B$) [5]. Some important issues, however, are still open to question.

One such issue is whether thermally assisted quantum tunneling, which has been observed for molecular magnets [3], exists in other nanomagnets with larger magnetic moments. The examined candidate was natural horse-spleen ferritin, which is an iron-storage protein. This protein has a spherical cage 8 nm in diameter containing polydispersive cores of antiferromagnetic ferrihydrite [4,6]. Each core has a small magnetic moment of $\sim 300 \mu_B$ due to its uncompensated spins [7,8]. At higher temperatures, the directions of such magnetic moments fluctuate thermally (superparamagnetic state) [7,8].

In 1995, it was observed that the temperature T_{max}, at which the dynamic susceptibility shows a maximum, increases as the magnetic field increases from 50 to 500 Oe [9]. It has been generally considered that T_{max} is proportional to the height of energy barrier. Because the barrier height for classical activated process decreases with the field, the increase of T_{max} was considered anomalous [10]. This behavior was explained by assuming the existence of thermally assisted resonant tunneling in the temperature region ~ 10 K [11]. However, a question as to the relationship between T_{max} and the barrier height immediately arose [12]. Numerical calculations showed that the variation of T_{max} is not always the same as that of the barrier height [12–14]. It was considered that the variation of T_{max} is affected by the field dependence of equilibrium magnetization M_{eq}, because observable magnetization is a product of M_{eq} and a factor relating to dynamics. Furthermore, it was pointed out that distribution $g(\tau)$ of the relaxation time τ must be taken into account, because T_{max} is sensitive to the width of $g(\tau)$. Thus, we cannot clarify the dynamics without information regarding both M_{eq} and $g(\tau)$. Therefore, Hanson *et al.* assumed M_{eq} and $g(\tau)$, and they pointed out that the anomalous field dependence of T_{max} can be almost explained by a classical model [12]. To this, Luis *et al.* replied using detailed numerical calculations [15], showing that the increase of the observed T_{max} with field is apparently faster than that predicted by the classical model if the assumptions concerning M_{eq} and $g(\tau)$ are improved. It is clear, however, that the controversy must reach a dead end at this point, because it is impossible to determine M_{eq} and $g(\tau)$ exactly unless all parameters of all particles are known. Hence, another approach that does not utilize T_{max} is desirable, in order to clarify whether the magnetic relaxations at the temperatures ~ 10 K are dominated by the quantum tunneling or not.

Sappey *et al.* responded to this need by proposing a more direct approach that combines field-cooled magnetization with a modified thermoremanent magnetization [16]. Although this approach showed dominance of the classical mechanism at higher fields, it could not clarify the mechanism in the field range below 1000 Oe. In this study, we note this remaining range, and discuss relaxation curves directly because the relaxation by the quantum tunneling slows down in fields H, while the classical relaxation accelerates in H [11].

Here we consider an isothermal magnetic relaxation from an equilibrium state in a field H_0 to another equilibrium state in another field H. In the initial state at a temperature T_0, the magnetization M_{eq} is given by $\sum m_j(H_0, T_0)$, where $m_j(H_0, T_0)$ is the expectation value of magnetization of the jth particle in the equilibrium in H_0. It should be noted that each $m_j(H_0, T_0)$ is an unknown function depending on the magnetic moment μ_j, the volume, and the orientation of the jth particle. If the initial field H_0 is cut off, relaxations in a zero field $H = 0$ can be observed. The magnetization $M(H = 0)$ during this process is given by

$$M(H = 0) = \sum_j m_j(H_0, T_0)\,(1 - r_j) \exp\left(\frac{-t}{\tau_j(H = 0)}\right), \tag{1}$$

where $\tau_j(H = 0)$ is the relaxation time of the jth particle in the zero field, and r_j is the reversible contribution due

to canting of the magnetic moment from the easy axis towards the field direction. The contribution due to canting immediately disappears after cutting H_0 because such variation needs no process through energy barriers. On the other hand, magnetic relaxations in a finite field $-H_0$ can be observed if the field is reversed from H_0 to $-H_0$. During this process, the magnetization $M(H = -H_0)$ varies from $M_{\rm eq}$ to $-M_{\rm eq}$:

$$M(H = -H_0) = -M_{\rm eq} + 2\sum_j m_j(H_0, T_0)(1 - r_j) \times \exp\left(\frac{-t}{\tau_j(H = -H_0)}\right), \quad (2)$$

where $\tau_j(H = -H_0)$ is the relaxation time of the jth particle in the field $-H_0$. The point is that the weights $m_j(H_0, T_0)$ in Eq. (2) are identical to those in Eq. (1), indicating that we can extract precise variations in dynamics due to the application of field by comparing the relaxation curves after cutting H_0 and after reversing H_0. This approach is not affected by the details of $m_j(H_0, T_0)$. Furthermore, it is not necessary to take into account the width of $g(\tau)$ when the half-lives $t_{1/2}$ of these relaxations are compared. The reason is that $t_{1/2}$ almost corresponds to the median of $g(\tau)$ even if a broad $g(\tau)$ exists [17].

The sample was a commercial ferritin from horse spleen (Wako Pure Chem. Ind. Ltd., 100 mg/cm^3). The solution was concentrated by drying in a vacuum desiccator. The concentration ratio is about 5 times. Magnetization was measured by using an extraction method below 150 K. The magnetization curve at 150 K indicates that each particle has a magnetic moment $\mu \sim 300\mu_{\rm B}$. Zero-field-cooled magnetization reaches a maximum at the temperature $T_{\rm max}$, which increases from 12.8 to 14.5 K as the applied field increases from 200 to 1000 Oe. These results are consistent with those reported previously [7–11].

We must first prepare an equilibrium state in a field H_0 as the initial state of relaxations described in Eqs. (1) and (2). In conventional studies, states after cooling in constant fields H_0 are usually used. In Fig. 1, the variation of magnetization $M_{\rm FC}$ after cooling in 200 Oe is shown as a function of time t after thermal stabilization at $T_0 = 8$ K. It can be seen that the magnitude of $M_{\rm FC}$ depends on the cooling rate. Furthermore, $M_{\rm FC}$ increases with time. These results indicate that the field-cooled states are far from the equilibrium. On the other hand, a prior study for iron-nitride nanoparticles has clarified that a nearly equilibrium state appears after cooling during which the ratio of H to T is fixed [18]. For this reason, such cooling conditions are examined here. A step-by-step cooling from 35 K to T_0 was employed with minimum intervals of 0.1 K. At every step, the applied field was changed to H_0T/T_0, where H_0 was the desired field of the initial state of relaxations at T_0. Figure 1 shows the magnetization M_{HT} after the cooling with H_0 of 200 Oe and with T_0 of 8 K. In contrast with $M_{\rm FC}$, M_{HT} is almost constant and is independent of the effective cooling rate. These results suggest that such states are close to equilibrium. Here we must

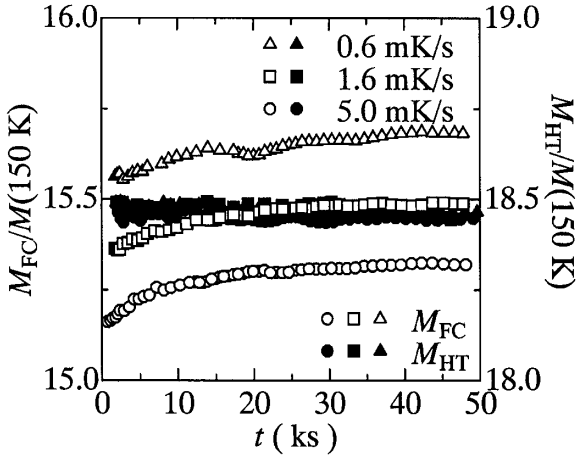

FIG. 1. Variation of magnetization at $H = 200$ Oe after thermal stabilization at $T = 8.0$ K. The cooling processes at various effective rates were carried out in $H = 200$ Oe ($M_{\rm FC}$) and in $H = 25T$ Oe (M_{HT}). The results are normalized by the magnetization at 150 K.

mention that no detectable variation was observed when the positions of the steps were changed, indicating that effects of the step-by-step cooling are negligible.

It is quite reasonable that an equilibrium state would appear after cooling during which the ratio of H/T is fixed, because the equilibrium states in lower fields are dominated by H/T. The reasons for this relationship are as follows. If nanomagnets are isotropic, such dominance is fully expected, since $m_j(H, T)$ is given by $L(\mu_j H/k_{\rm B}T)$, where $L(x)$ is the Langevin function. The existence of the energy barrier, however, proves that the ferritin is magnetically anisotropic. In such cases, the direction of the magnetic moment $\boldsymbol{\mu}$ is trapped at the bottom of one of the wells parallel to the easy axes at temperatures below blocking temperature $T_{\rm B}$, because the depth of each well is approximately 25 times greater than the thermal energy at $T_{\rm B}$. Because the relative energy levels of the bottoms are given by $-\mu H\cos\psi$, the population of each well is determined by $\mu H\cos\psi/k_{\rm B}T$, that is, H/T, where ψ is the angle from the direction of $\boldsymbol{H}$ to the direction of the easy axis. Therefore, the equilibrium state above $T_{\rm B}$ can be preserved without a shift in population between the wells during cooling. For example, a numerical calculation shows that such a shift is less than 1% when uniaxial nanomagnets are cooled from $T_{\rm B}$ to $(1/3)T_{\rm B}$.

We are now in a position to discuss the magnetic relaxations themselves at T_0, because the equilibrium state in H_0 can be prepared. Before comparing the two curves described in Eqs. (1) and (2), the temperature dependence of magnetic relaxations should be clarified, since it has also been discussed by utilizing $T_{\rm max}$. Figure 2 shows observed relaxation curves of $M(H = 0)$ at various T_0 after cooling during which the ratio of H to T was fixed at 25 Oe/K. If the state is preserved during the cooling, as discussed above, the initial states of these curves are the same. Actually, the initial states satisfy this condition, because the

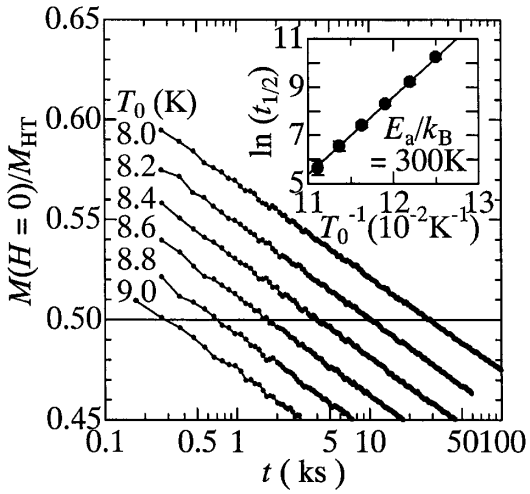

FIG. 2. Relaxation curves in a zero field at various temperatures. The initial states were created by cooling during which the ratio of H to T was fixed at 25 Oe/K. The curves are normalized by the initial value M_{HT}. The inset shows the temperature dependence of the half-life $t_{1/2}$ of the relaxation.

variation of M_{HT} is less than 0.5% in the concerned temperature range between 8 and 9 K. Because their final states are also the same, differences between them can be attributed to variations in dynamics. In Fig. 2, we find that the curves have linear dependence on ln$t$. The slope of the relaxation curve is discussed later, and we should note that the position shifts toward short time with increasing temperature. This behavior clearly indicates an acceleration of relaxation due to thermal energy. The inset of Fig. 2 shows the temperature dependence of the half-life $t_{1/2}$, which is the time when $M(H = 0)/M_{HT} = 1/2$. It can be clearly seen that $t_{1/2}$ has an exponential dependence on $1/T_0$, where the activation energy E_a/k_B is approximately 300 K. From this value, effective anisotropy field H_K for $\boldsymbol{\mu}$ is estimated at $2E_a/\mu \sim 30$ kOe. As discussed here, thermal excitations dominate the dynamics.

Next, we return to the issue of the field dependence of magnetic relaxations, in order to clarify whether the dynamics is dominated by thermally assisted quantum tunneling, or by classical activated process. As discussed at the beginning of this report, we can extract the variations in dynamics due to the field by comparing the relaxation curves after reversing H_0 and after cutting H_0. In Fig. 3, open circles show $M(H = -H_0)$ after reversing H_0, while filled circles represent $M(H = 0)$ after cutting H_0. These curves are normalized by the initial value M_{HT}, where the field dependence of M_{HT} can be explained by a superparamagnetic model [19] for the following values: $E_a/k_B \sim 300$ K and $\mu \sim 300\mu_B$. It can be seen in Fig. 3 that the difference between the two curves is small at lower H_0. In contrast, at higher H_0, the position of the relaxation curve at $H = -H_0$ seems to shift toward short time, in comparison with the curve at $H = 0$.

Before coming to any conclusions, we should examine the assumptions used in this analysis, because the observed

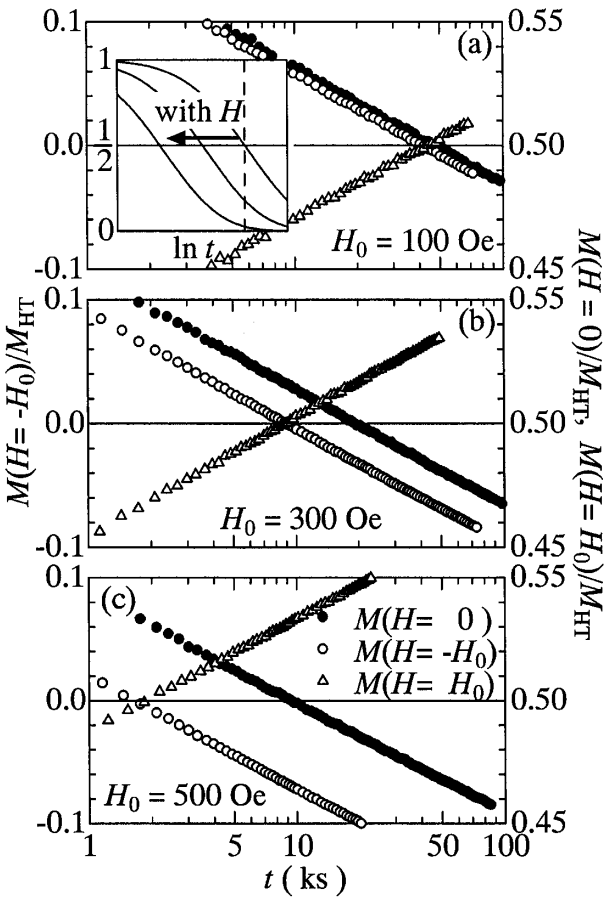

FIG. 3. Relaxation curves in various fields at $T_0 = 8.0$ K. The open and filled circles represent $M(H = -H_0)$ and $M(H = 0)$, respectively, after cooling during which the ratio of H to T is fixed at H_0/T_0. The triangles show $M(H = H_0)$ after cooling in a zero field. The curves are normalized by the initial value M_{HT} of $M(H = 0)$. The inset shows a sketch of the whole curve.

difference between the two curves is only a few percentage points. Two points are debatable. One is that the same factor $1 - r_j$ is employed in Eqs. (1) and (2) because the reversible contribution r_j for the field variation from H_0 to 0 is not completely equal to half that for the variation from H_0 to $-H_0$. Such a difference in r_j is, however, negligible when H_0 is sufficiently small in comparison with the anisotropy field H_K. If H_K is assumed at 30 kOe, the difference in r_j for uniaxial nanomagnets is much smaller than 0.1% in the range below 1 kOe. The other point regards the assumption $M_{HT} \approx M_{eq}$. Although it has already been shown that M_{HT} is constant in the finite period of 50 ks, this may be too short a period to predict the equilibrium state. Therefore, we must consider the third type of relaxation. When the field $H = H_0$ is applied after the cooling to T_0 in a zero field, magnetization $M(H = H_0)$ is expressed as

$$M(H = H_0) = M_{eq} - \sum_j m_j(H_0, T_0)(1 - r_j) \times \exp\left(\frac{-t}{\tau_j(H = H_0)}\right). \quad (3)$$

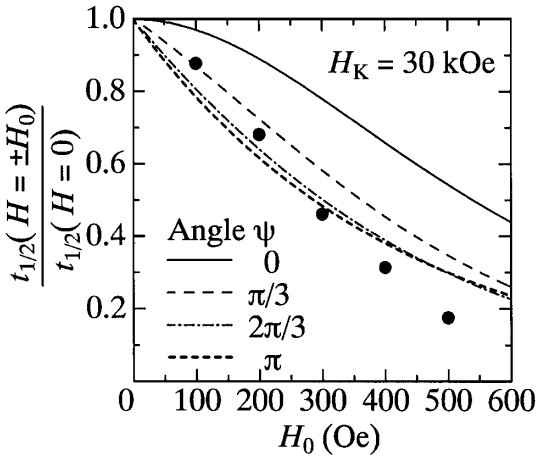

FIG. 4. Ratio of the half-life $t_{1/2}$ of the relaxation in finite fields $\pm H_0$ to $t_{1/2}$ in a zero field. The lines are calculated using a classical model.

The comparison between Eqs. (3) and (2) shows that the second terms are the same, because $\tau_j(H = H_0) = \tau_j(H = -H_0)$. For this reason, $t_{1/2}(H = H_0)$ should be identical to $t_{1/2}(H = -H_0)$ if $M_{HT} = M_{\rm eq}$, where $t_{1/2}(H = H_0)$ is the time when $M(H = H_0)/M_{HT} = 1/2$, and $t_{1/2}(H = -H_0)$ is the time when $M(H = -H_0)/M_{HT} = 0$. In contrast, a discrepancy between $t_{1/2}(H = H_0)$ and $t_{1/2}(H = -H_0)$ is expected when $M_{HT} \neq M_{\rm eq}$, because they are not true half-lives. The triangles in Fig. 3 show $M(H = H_0)$ as a function of time after applying H_0. The above condition is clearly satisfied. Hence, the latter assumption, $M_{HT} \approx M_{\rm eq}$, is valid. Therefore, we are certain that variation in dynamics causes the difference between the two curves, that is, the shift of position. In order to clearly show the shift, the ratio of $t_{1/2}(H = \pm H_0)$ to $t_{1/2}(H = 0)$ is plotted in Fig. 4. It can be seen that the relaxation is accelerated by applying a field in a range below 500 Oe, as behavior that is contrary to that expected for thermally assisted quantum tunneling.

Let us compare the results obtained here with theoretical predictions for classical activated process. Useful expressions have been given for the relaxation time τ_1 which corresponds to the lowest nonvanishing eigenvalue of the Sturm-Liouville equation [20]. The lines in Fig. 4 show τ_1 calculated for various ψ, where ψ is the angle from the direction of $\boldsymbol{H}$ to the direction of the easy axis. Low damping is assumed here. It is found that the ratios of $t_{1/2}(H = \pm H_0)$ to $t_{1/2}(H = 0)$ are roughly consistent with the calculated curves. Thus, the observed shift of the relaxation curve due to the field can be interpreted by using a classical model of superparamagnetic fluctuations.

Finally, we discuss the slope of the relaxation curve, which corresponds to the magnetic viscosity S. In each figure, the slope is almost constant. For example, the ratio of the slope of $M(H = -H_0)$ to that of $M(H = 0)$ is 0.98×2 in Fig. 3(c). This result indicates that $S(t = t_{1/2})$ is independent of the field in the range below 500 Oe. Is this dependence inconsistent with the decrease of S observed in previous studies [11,15]? In order to answer the question, a sketch of the whole curve is given in the inset of Fig. 3(a), where it shifts without variation of shape. We should notice that $S(t = t_{1/2})$ obtained in the window along the solid line at $1/2$ is constant, whereas S obtained in the vicinity of a fixed time has an apparent variation (see the broken line). For this reason, we can accept little variation of the shape in the narrow range below $H \sim 0.02 H_K$. Similarly, little variation of $S(t = t_{1/2})$ in the range from 8 to 9 K can be explained. As described in this study, the magnetic relaxations of ferritin in magnetic fields are dominated by classical superparamagnetic fluctuations in the temperature regime where thermally assisted quantum tunneling has been discussed in recent years.

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