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Contribution of Langevin behavior to the low temperature maximum in zero-field cooled magnetization of the discontinuous Fe films

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The dominant factor of low temperature maximum of zero-field cooled (ZFC) magnetization has been investigated using a discontinuous ultrathin Fe film which is superparamagnetic at room temperature. The peak temperature of ZFC magnetization increases with increasing magnetic field strength, contrary to the Nèel-Brown model. It is explained by the Langevin behavior of superparamagnetic particles dominating the low temperature maximum of ZFC magnetization due to the wide energy barrier distribution. For the case, the peak temperature should not be a good estimation of the blocking temperature since thermal activation of magnetization does not have a significant role in the low temperature maximum of ZFC magnetization. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2830948]

Magnetization of nanosized magnet is fluctuated due to the thermal agitation and the highly fluctuating magnetization results in superparamagnetism. Partly owing to the development of magnetic storage devices, the thermal fluctuation of magnetization and the superparamagnetism are currently the subjects of intense research activity. As one topic in this research field, the qualitative estimation of thermal stability of magnetization is lively studied through the effective energy barrier of magnetization rotation and the magnetization relaxation path in three dimensional energy landscape.[1–4] Especially for the superparamagnetic system, the thermal stability of magnetization is discussed using the blocking temperature, which is often estimated from the peak temperature of zero-field cooled (ZFC) magnetization. However, the peak temperature of ZFC magnetization does not always represent the blocking temperature in the presence of energy barrier distribution. This is because the estimation using the peak temperature of ZFC magnetization assumes that the low temperature maximum of ZFC magnetization is dominated by the thermal activation across the energy barrier. Actually, the thermal activation of magnetization is significant just for the particle having the energy barrier, $\Delta E \propto K_{\mathrm{eff}}V \approx \ln(t_m/\tau_0)k_BT$, where K_{eff} is the effective magnetic anisotropy, V is the volume, t_m is the measurement time $\approx$100 s, τ_0 is the prefactor $\approx 10^{-9}-10^{-12}$ s. In an actual system, there is inevitably a size distribution, more precisely an energy barrier distribution. The size/energy barrier distribution is schematically shown in Fig. 1. In the figure, the log-normal distribution is presented as the general size distribution. In the presence of the energy barrier distribution, the thermal activation of magnetization is significant for a part of distribution in which the energy barrier is comparable to the thermal energy within the measurement time $\approx \ln(t_m/\tau_0)k_BT$. The magnetizations of other type of particles having $\Delta E \ll (\gg) \ln(t_m/\tau_0)k_BT$ are highly fluctuated (stable) and, thus, they behave as a superparamagnet (a ferromagnet), respectively. The former type of particle contributes to the measured magnetization in the manner of the Langevin function, hereafter we call the magnetic behavior expressed by the Langevin function as the Langevin behavior, and the latter as the magnetization rotation. Especially in a wide energy barrier distribution, either of these types of magnetic behavior could dominate the measured magnetization instead of the thermal activation. As a consequence, the peak temperature of ZFC magnetization does not represent the blocking temperature anymore, and has a different physical meaning. In the present study, we focus on clarifying the physical meaning of the low temperature maximum of ZFC magnetization using magnetic nanoparticles fabricated by the Volmer-Weber growth of ultrathin film. The Volmer-Weber growth of ultrathin film has the ability to create a two dimensionally aligned nanoparticle assembly and to alter the crystallographic orientation of particles via the epitaxial growth.

We chose Fe grown on α-$Al_2O_3(0001)$ substrate for investigation system because Fe has the highest saturation

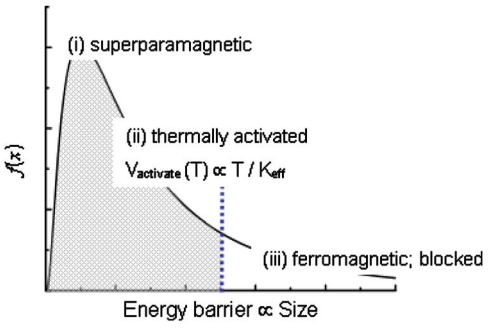

FIG. 1. (Color online) Schematic representation of size/energy barrier distribution. The thermal activation is significant for a part of distribution, $\Delta E \propto K_{\mathrm{eff}}V_{\mathrm{activation}} \approx \ln(t_m/\tau_0)k_BT$. Below the activation volume $V_{\mathrm{activation}}$, the particles behave as the superparamagnet (the hatched region).

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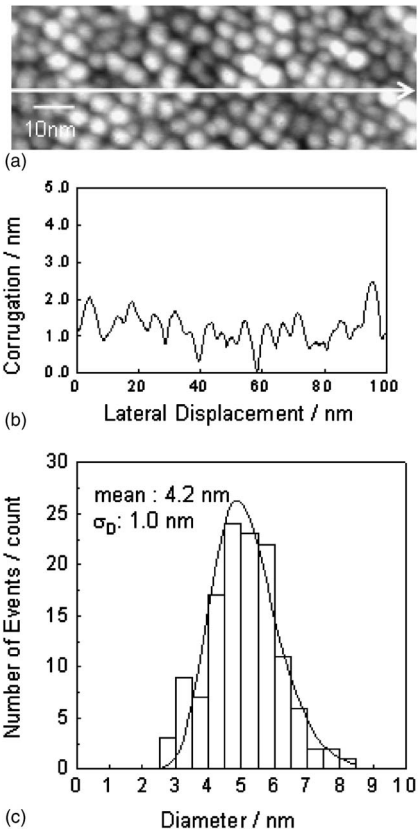

FIG. 2. AFM image of ultrathin Fe films on α-Al_2O_3(0001) and the diameter distribution of Fe particles estimated from AFM images.

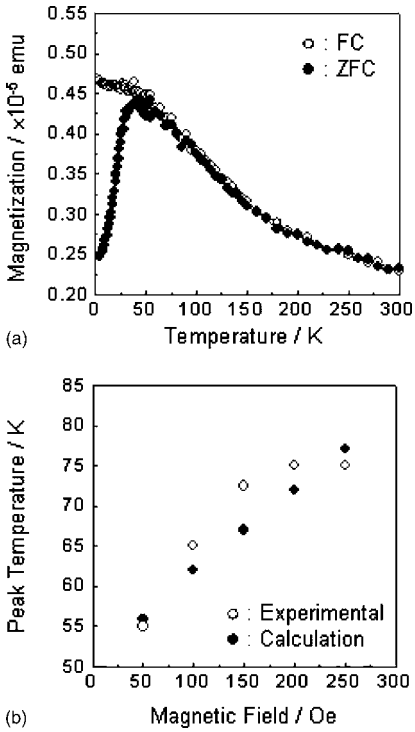

FIG. 3. (a) Temperature dependence of magnetization. The open and closed circles represent the values of field-cooled (FC) and zero-field cooled (ZFC) magnetization, respectively. (b) Field dependence of peak temperature of ZFC magnetization. The open and closed circles represent the experimentally obtained and the calculated values, respectively (see text).

magnetization in the single element magnets, which helps the magnetization measurement, and α-Al_2O_3 is a suitable substrate for forming the discontinuous ultrathin film.[5–7] Ultrathin Fe film was prepared by molecular beam epitaxy (MBE) using a VG-80M MBE system. The pressure before and during the deposition was typically $<4\times10^{-9}$ and 5×10^{-8} Pa, respectively. The nominal thickness of Fe was fixed at 1.0 nm and the growth temperature was fixed at 573 K. The magnetic properties were investigated by means of the superconducting quantum interference device magnetometry. Our investigation encompassed the temperature dependence of FC magnetization, ZFC magnetization, and remanent magnetization (RM) in the temperature range of 10–300 K. The measurements were performed during the heating process. FC and ZFC magnetizations were measured under the in-plane magnetic fields from 50 to 250 Oe. Two types of RM are measured after FC and ZFC, called as the thermoremanent magnetization (TRM) and the isothermal remanent magnetization (IRM), respectively.[8,9] TRM (IRM) was measured after measuring FC (ZFC) magnetization and removing the magnetic field, respectively. For instance, when TRM was measured, the sample was cooled from the high enough temperature, 300 K to the measurement temperature under the certain field. After reaching measurement temperature, the field was removed and the magnetization was measured. In the case of IRM, the similar procedure was done after ZFC procedure. TRM and IRM give the magnetizations from the magnetically stable particles and the thermally activated particles at the measurement temperature, respectively. To investigate the magnetic properties, the Fe films have to be exposed to air. In order to avoid the surface oxidization, a 10-nm-thick Au capping layer was deposited at room temperature (RT). We confirmed the lack of oxidation indirectly from the fact that the magnetization curves at 10 K show no shift after cooling in field (10 kOe). The surface structure of the Fe film was investigated *in situ* by means of noncontact atomic force microscopy (AFM). As shown in Fig. 2, Fe particles are formed on α-Al_2O_3(0001) by the Volmer-Weber growth. The mean diameter of particles is 4.2 nm and the standard deviation of particle distribution is 1.0 nm. The shape of diameter distribution is nearly the log-normal distribution shown by the solid line and, thus, the situation explained above is valid for our system.

The temperature dependence of FC and ZFC magnetizations are shown in Fig. 3(a). Two characteristic features showing that our sample is superparamagnetic at RT are clearly seen in the figure, i.e., the difference between FC and ZFC magnetizations and the low temperature maximum in the ZFC magnetization. Additionally, the fact that the magnetization curve at RT (not shown) is well represented by Langevin function supports the superparamagnetic state of Fe.[10] In Fig. 3(b), the field dependence of the peak temperature is shown. Note that even though ZFC magnetization was measured after zero-field cooling procedure, the infinite magnetic field was applied during the measurement. According to the Néel-Brown model, namely, the thermal activation model, the peak temperature has to decrease with increasing magnetic field since the energy barrier for the magnetization rotation from the metastable state to the equilibrium state

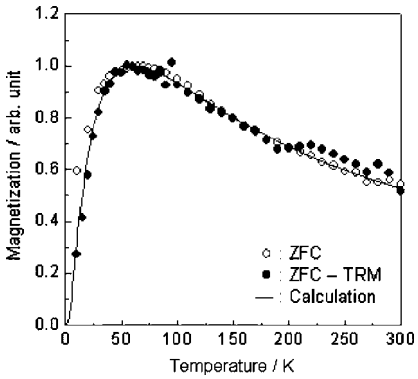

FIG. 4. Calculated temperature dependence of magnetization using Langevin function (solid line). As references, the ZFC magnetization and the difference of ZFC magnetization and TRM, ZFC magnetization; TRM are shown by the open and closed circles, respectively.

decreases due to the Zeeman energy. However, it is clearly seen in Fig. 3(b) that the peak temperature increases with increasing field strength contrary to the above expectation. Thus, the observed feature indicates that the low temperature maximum of ZFC magnetization is not dominantly affected by the thermal activation of magnetization. In order to explain the results and to clarify the dominant factor of ZFC magnetization, we focused on the superparamagnetic response of particles having the lower energy barrier (hatched region in Fig. 1) as the other contribution from the thermal activation. The magnetic behavior of superparamagnetic particle is represented by the Langevin function. Hence, the whole contribution of the particles having the lower energy barrier is accessible to integrate the Langevin function within the superparamagnetic region (hatched region in Fig. 1).[11] By using the following formula, we have calculated the ZFC magnetization:

$$M_{\mathrm{ZFC}} = \int_0^{V_{\mathrm{activate}}(T)} M(x),$$

$$V_{\mathrm{activate}}(T) = \frac{25k_BT}{K_{\mathrm{eff}}},$$

$$M(x) = M_S \frac{\pi}{6} x^3 f(x) dx L(a),$$

$$L(a) = \coth(a) - \frac{1}{a},$$

$$a = M_S \frac{\pi}{6} x^3 H/k_BT, \tag{1}$$

where K_{eff} is the effective magnetic anisotropy energy (here, we assume the bulk magnetocrystalline anisotropy, 4.7×10^4 J/m^3 for simplicity), M_S is the saturation magnetization (2.1 T), x is the particle diameter, $f(x)$ is the probability function of particle diameter, $L(a)$ is the Langevin function, k_B is the Boltzmann constant, and T is the absolute temperature. The calculated result is shown in Fig. 4(a) as a solid line. As clearly seen, Langevin function alone generates the low temperature maximum in the ZFC magnetization. It is worthy to note that the low temperature maximum is not generated by the only linear term of Langevin function but by the combination of the nonlinear term of Langevin function and the size/energy barrier distribution. The calculated results correspond well to the experimentally obtained ZFC magnetization [Fig. 4(a), open circles] above the peak temperature. The slight deviation in the low temperature regime is due to the contribution from magnetization rotation of blocked particles, which is obtained as TRM. In fact, the subtracted signal, ZFC magnetization – TRM [Fig. 4(a), closed circles], is comparable to the calculated results in the whole temperature range. Besides the temperature dependence of the ZFC magnetization, the calculated peak temperature increases with the field strength and also agrees with the experimental results qualitatively [Fig. 3(b), closed circles]. Note that the parameters used in the calculation except for the magnetic field strength are exactly the same for all calculations. As explained above, since our model includes only the Langevin behavior, i.e., the contribution from the superparamagnetic particles, the agreement between the experimental results and the calculated results strongly indicates that the ZFC magnetization is dominated by the Langevin behavior of superparamagnetic particles. The thermal activation of magnetization does not affect the measured magnetization crucially around the peak temperature of ZFC magnetization and, thus, the peak temperature would not represent the superparamagnetic blocking temperature.

In summary, we have investigated the dominant factor of low temperature maximum of ZFC magnetization of the superparamagnetic ultrathin Fe film. In the presence of size/energy barrier distribution, the magnetic behavior other than the thermal activation could dominate the ZFC magnetization. Especially, in our case, Langevin behavior of superparamagnetic particles dominates the ZFC magnetization more than the thermal activation. In this case, the peak temperature increases with increasing magnetic field, which cannot be explained by the thermal activation model of magnetization.

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