Possibility of a correlation-spectroscopy study of small ferromagnetic particles

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Small ferromagnetic particles can be studied by a method of correlation spectroscopy. The dispersion of small superparamagnetic particles of Fe_3O_4 has been studied. Measurements of the correlation function of the light intensity scattered by this system have made it possible to determine the spontaneous magnetization-reversal time and also the anisotropy constant of the particles over the conventional method for studying superparamagnetism—Mössbauer spectroscopy—are discussed.

It has become extremely urgent to study small ferromagnetic particles theoretically and experimentally. This research is of practical importance because of the widespread use of the dispersion of these particles in carriers for magnetic recording.[1] A topic of independent theoretical interest is the size dependence of the physical characteristics of ferromagnets (the anisotropy constants, etc.).[2]

As the size of these particles decreases, they go into a so-called superparamagnetic state: Although the moments of the individual atoms remain collinear (a ferromagnet), the resultant moment of a particle undergoes a spontaneous change in direction with respect to the crystallographic axes, since the thermal fluctuations reach a level on the order of the magnetic anisotropy energy.[2] The average time for the magnetization reversal of a particle in the absence of external fields is called the "spontaneous magnetization reversal time" τ_r.

Essentially the only way to study superparamagnetism is Mössbauer spectroscopy,[3] where the contribution of superparamagnetic relaxation to the spectrum leads to a broadening and coalescence of Mössbauer lines as the temperature is raised. In the present paper we show that it is possible to study this phenomenon by the method of "correlation spectroscopy," and we discuss certain advantages of this method.

The method of correlation spectroscopy can be outlined as follows[4]: In ordinary spectroscopy, a spectrum analyzer (a prism, etc.) is placed in the path of the scattered radiation, and a photodetector (a photographic plate) is placed behind it. The detector records the spectrum of the scattered light. In the method of correlation spectroscopy, in contrast, the scattered light first strikes the photodetector (a photomultiplier), and a spectrum analyzer or correlator is placed at the exit from the detector. The analyzer or correlator measures the spectrum of fluctuations in the photocurrent of the detector or constructs its temporal correlation function $G(t) = \langle I(0)I(t)\rangle$ [$I(t)$ is the output current of the photomultiplier at time t]. Under certain conditions, this fluctuation spectrum and its temporal correlation function are the same as, respectively, the fluctuation spectrum and the correlation function of the intensity of the scattered light

(the decay time of the correlation function, τ_c, is the relaxation time of the fluctuations which affect the scattering in the system). Because of the quadratic nature of the detection (the photomultiplier removes the carrier frequency), the spectrum of the signal under study is shifted toward the origin of the frequency scale (into the frequency band 0–10^8 Hz). The signal can thus be analyzed by electronic methods, and very small spectral shifts of the scattered light (1–10^7 Hz) can be studied; i.e., it is possible to study very slow changes (with a scale time of 10^{-7}–1 s), which are beyond the scope of ordinary spectroscopy.

The interaction of the incident radiation with the magnetic moment of a particle leads to fluctuations in the scattered field upon a spontaneous magnetization reversal of the particles. As a result, the correlation function of the intensity of the scattered light carries information on the magnetization reversal time τ_r.

In the absence of other fluctuations (Brownian motion, etc.), the decay time of this correlation function is simply τ_r, since a spontaneous magnetization reversal is the only process which would contribute to the correlation function. To prove that this process is observed experimentally, it is simplest to study the dependence of τ_c on the magnitude of the magnetic field applied to the sample, since the effect of this field on processes which are unrelated to the relaxation of the magnetic moment is small.

For simplicity, we consider an ensemble of particles with an easy-axis anisotropy; the axes of easy magnetization of the particles are oriented along the magnetic field. We assume that the anisotropy energy U_{an} is comparable to the energy of the thermal fluctuations ($U_{an} = KV_0\sin^2\alpha$, where K is the anisotropy constant, V_0 is the volume of a particle, and α is the angle between the easy axis and the moment; at equilibrium, we would have $\alpha = 0$). In the absence of an external field, the moment of a particle would then have two equilibrium positions of equal standing (both directions along the easy axis), which are separated by a potential barrier. The average time for a transition from one position to the other is τ_r. The imposition of an external field causes the orientation along the field to become preferred. Two types of transitions then arise: a transition from the state along the field to the state opposite the field ($\uparrow\uparrow \rightarrow \uparrow\downarrow$) and the inverse transition. If the external field H causes only a slight distortion of the potential barrrier ($\mu H \ll U_{aH}$, where μ is the moment of the particle), the times of these transitions are related to τ_r by (see Ref. 5 for a detailed discussion)

$$\tau_{\uparrow\downarrow\rightarrow\uparrow\uparrow} = \tau_r e^{-\mu H/kT} \qquad \tau_{\uparrow\uparrow\rightarrow\uparrow\downarrow} = \tau_r e^{\mu H/kT}.$$

Here we have[2] $\tau_c = \tau_0 \exp(KV_0/kT)^2$; i.e., the transition $\uparrow\downarrow \rightarrow \uparrow\uparrow$ is an exponentially faster process. At early times, this transition thus dominates the correlation function, and its decay time depends exponentially on H:

$$\ln\tau_c = \ln\tau_r - \frac{\mu}{kT}H = \ln\tau_0 + \frac{KV_0}{kT} - \frac{\mu}{kT}H, \qquad (1)$$

This theory also is qualitatively correct for the case of a nonuniaxial anisotropy or if there is some spread in the directions of the easy axes.

The experimental arrangement is shown in Fig. 1. The light source is He-Ne laser with a power of 35 mW. The depolarized component of the scattered light is measured in order to reduce the background (P is a polarizer and A is an analyzer). The correla-

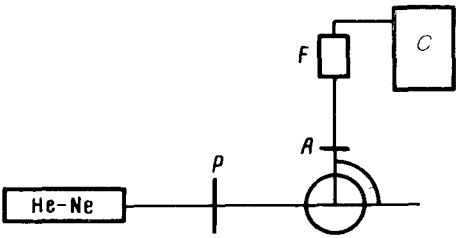

FIG. 1. The experimental arrangement.

tion function of its intensity is calculated by a Kh6-4 correlator C. The sample, held in a constant-temperature cell ($27.0 \pm 0.1°$ C), is a suspension of Fe_3O_4 particles (with a cubic anisotropy) "frozen" in an epoxy matrix (to eliminate any effect of diffusion). The epoxy resin is solidified during a dispersal in an ultrasonic bath in order to achieve a uniform distribution of the particle over the volume and to reduce clustering. The particles make up a fraction $\sim 10^{-3}$–10^{-4} of the volume, so that the interaction between particles can be ignored. A coil is wound around the cell which holds the sample in order to impose an external field. The current in this coil is provided by a regulated B5 power supply. The current can be varied over the range 0–2.5 A; correspondingly, H can be varied over the range 0–12 Oe.

The experimental results are shown in Fig. 2. The dependence of the logarithm of the decay time of the correlation function, τ_c, on H (Fig. 2b) can be approximated well by a straight line; this result is evidence that relation (1) holds. From the slope of this line we find the value $a = \mu/kT \approx 0.31$ G^{-1}; hence the average moment of the particle is $\mu \sim 1.4 \times 10^{-14}$ erg/G. An extrapolation of the straight line to the ordinate yields an intercept $\tau_r \approx 1.1 \times 10^{-2}$ (this determination is more accurate than a determination from the correlation function in the absence of a field because of the effect of random magnetic fields in the latter case).

From these results we can estimate the first anisotropy constant and the average diameter of the particles. Here we can write[6]

$$\tau_r = \frac{I_s \sqrt{\pi}}{K\gamma_0} \left(\frac{KV_0}{kT} \right)^{-1} e^{KV_0/kT} . \qquad (2)$$

Using the notation $x = KV_0/kT$, and substituting τ_r and a into (2), we find from the transcendental equation

$$x^{-3/2} e^x = \tau_r \gamma_0 / a \sqrt{\pi}$$

for x (γ_0 is the gyromagnetic ratio) the value $x \approx 17$. Using the known magnetization[6] of Fe_3O_4, $I_s = 471$ G, and the relation $\mu = I_s V_0$, we can estimate the particle diameter, $D \sim 40$ nm, and the constant K, $\sim 3 \times 10^4$ erg/cm^3. The results agree well with data from electron microscopy and data from the literature on K (Ref. 6).

The method of correlation spectroscopy has some important advantages over Mössbauer spectroscopy: its simplicity, the graphic form of the results (τ_r is measured directly), and the possibility of studying the superparamagnetism of materials which have no Mössbauer isotopes.

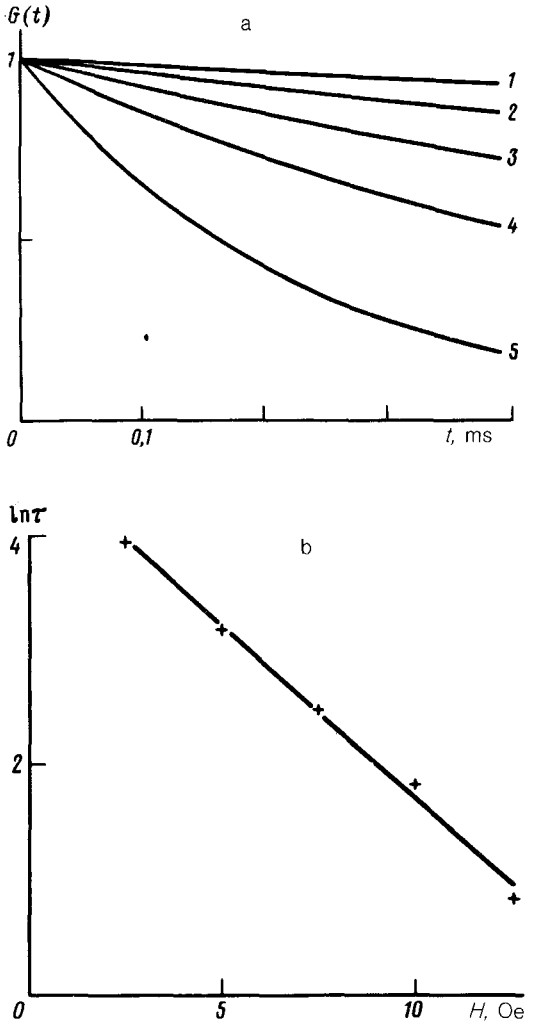

FIG. 2. a: Change in the correlation function as H is increased. 1—$H = 2.5$ Oe; 2—$H = 5$ Oe; 3—$H = 7.5$ Oe; 4—$H = 10$ Oe; 5—$H = 12.5$ Oe. b: Logarithm of the decay time of the correlation function versus H.

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