Memory effects in superparamagnetic La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticles

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Abstract. Using different temperature and field protocols, the memory behaviors in the dc magnetization and magnetic relaxation are observed at temperature below blocking temperature $T_B = 93$ K in weakly interacting manganite La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticles. The results indicate that the magnetic dynamics of this nanoparticle system is strongly correlated with a wide distribution of particle relaxation times, which may arise from the particle weak interaction and distribution of the particle size.

1 Introduction

The slow dynamics, including non-exponential relaxation, aging $^{[1,2]}$, and memory effects $^{[3,4]}$, has been one of the hot topics in the field of condensed matter physics in the past several decades. These phenomena are observed in various systems such as granular materials $^{[5]}$, high-$T_c$ superconductors $^{[6]}$, polymers $^{[7]}$, and interacting (non-interacting) magnetic nanoparticles $^{[3,4]}$. The magnetic moment of the nanoparticle generally consists of a single-domain structure of ferromagnetic spins, whose orientation depends on the magnetic anisotropy and the effective magnetic field. For a non-interacting assembly of magnetic nanoparticles the dynamics is typically described by the Neel-Brown theory $^{[8,9]}$. The relaxation time, $\tau(T) = \tau_0 \exp(KV/k_BT)$, of the magnetic moment of an individual magnetic particle is only governed by its own anisotropy energy at a given temperature $T$, where $\tau_0$ is the microscopic time; $k_B$ is the Boltzmann constant; $K$ and $V$ are the anisotropy constant and the volume of particle, respectively $^{[10]}$. The relaxation time increases exponentially with decreasing temperature, and when $KV/k_BT \geq 25$ the magnetic moment is frozen in one direction of its easy axis, the flip of the moment is blocked, and the relaxation time equals the measuring time at the blocking temperature $T_B$ corresponding to the peak position of zero-field-cooled (ZFC) curve. At high temperatures, the moment flipping between two directions of its easy axis is described by superparamagnetic model.

As for the interacting nanoparticles, the dipole-dipole interactions will affect the dynamics of the magnetic moment. If the interaction is not very strong, the dynamics of each magnetic moment can still be described by a superparamagnetic model, but with a modified energy barrier $^{[10]}$. Recently, memory effects have been found in many magnetic particle systems $^{[3,4,10–14]}$, also in phase separated bulk and thin film manganites $^{[15–17]}$, but seldom reported in nanosized manganites.

Manganites have attracted much attention because of the rich physics and the potential application in magnetic storage and spintronic devices $^{[18]}$. Among the manganite systems, $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ with Curie temperature above room temperature has a great potential application in spintronic devices working at room temperature $^{[19]}$. Recently, the size effect on magnetic properties of $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ has been reported $^{[20]}$. With reducing particle size the magnetic structure of particles evolves from magnetic multi-domain to single domain, and finally a superparamagnetic behavior is detected for a sample with particle size about of 5 nm. In the present work, $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ with average particle size about of 5 nm was studied using different temperature and field protocols, the similar memory behavior to that in $\gamma\text{-Fe}_2\text{O}_3$ $^{[3]}$, $\text{Ni}_{81}\text{Fe}_{19}$ $^{[11]}$, $\text{Fe}_3\text{N}$ and ferritin $^{[4]}$ in the dc magnetization and magnetic relaxation has been observed at temperature below its blocking temperature $T_B = 93$ K. These memory effects may have important device applications in the future $^{[21]}$.

2 Experimental

The samples used in the experiments were prepared by a sol-gel method $^{[19]}$. The X-ray powder diffraction pattern, shown in Figure 1, indicates that the synthesized sample by annealed at 250 °C is perovskite structure $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ nanoparticles and some organic precursors, indicated by the broad protrusion around 30 degree, as compared with the corresponding bulk compound.

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The average particle size of the nanoparticles is about 5.1±0.4 nm determined by the widths of the diffraction peaks using Scherrer formula. The composition is checked by the inductively coupled plasma atomic-emission spectroscopy techniques, within the experimental uncertainty the result is in agreement with the nominal composition (molar ratio of La:Pb:Mn = 3:2:5). The oxygen stoichiometry was checked by K$_2$Cr$_2$O$_7$ and FeSO$_4$ titration for three times. The results indicate that the oxygen content (3 − δ with δ = 0.018 ± 0.004) is very close to 3. The dc magnetization measurements were performed using a superconducting quantum interference device (SQUID). The saturated magnetic moment at 30 K, obtained by extrapolation of the $M$ vs. $H$ data to 1/$H = 0$, is 2.8 emu/g, which is about 41% of the saturation magnetization of bulk La$_{0.6}$Pb$_{0.4}$MnO$_3$ [20]. As compared with the result in reference [3], the $M$ vs. $H$ should not be lower than 45% $M_{s}$, bulk if the concentration of La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticles is 100% in sample. From the $M_s$ value one can estimate that the proportion of the La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticle is about 9%, which implies that the La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticles embedded in the organic precursor and the interparticle interaction is very weak.

3 Results and discussions

Figure 2 shows the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations, measured as a function of temperature (10−350 K) at a magnetic field $H = 100$ Oe for the studied sample. The curves exhibit a typical characteristic of a superparamagnetic system; i.e., the ZFC curve has maximum at the blocking temperature $T_B = 93$ K, while the FC curve continues to increase with decreasing temperature [4,11]. According to $KV \approx 25k_BT_B$, the average anisotropy constant $K \approx 4.9 \times 10^5$ erg/cm$^3$ can be estimated, which is larger than that of superparamagnetic γ-Fe$_2$O$_3$ nanoparticles in reference [3]. The superparamagnetic behavior was confirmed by magnetic hysteresis measurements at both above and below $T_B$, as shown in the inset (a) of Figure 2. The hysteresis appears below blocking temperature while it is absent above $T_B$. In addition, the absence of the dependence on the waiting time for the ZFC magnetization relaxation rate $S = dM/d\ln(t)$ also confirms the superparamagnetic nature [3], as shown in the inset (b) of Figure 2. Therefore, one can conclude that our system is weakly interacting or noninteracting.

In order to investigate the low-temperature dynamics of the FC magnetization of as-prepared La$_{0.6}$Pb$_{0.4}$MnO$_3$ nanoparticles below $T_B$, an approach similar to that used by Sun et al. [11] and Tsoi et al. [3] was employed. The sample is cooled in $H = 100$ Oe from 300 down to 10 K and then the magnetization was recorded during the heating. The obtained $M(T)$ curve is referred as the reference curve and is shown as red square in Figure 3. Then the sample is cooled again at the same rate and the magnetization is recorded during the cooling, but now with temporary stops at $T = 40$ and 20 K for the identical waiting times $t_{W} = 4$ h, respectively. During $t_{W}$, the field is switched off to let the magnetization relaxes downward. After each stop and waiting period, the 100 Oe field is reapplied and cooling is resumed. This cooling procedure produces a step-like magnetization curve as shown by the black solid square symbols in Figure 3. After reaching 10 K, the sample is reheated at the same rate in $H = 100$ Oe and the magnetization is recorded again (open green circles). The system clearly remembers its thermal history as the curve reproduces the step-like shapes nearby the temperatures where the system was stopped during the cooling process; moreover, the magnetization during warming recovers the cooling $M(T)$ curve within several Kelvin of the appearance of the steps. This is the so called memory effect. In order to further verify the memory effect, the ZFC magnetization relaxation itself and the influence of a temperature change on the relaxation behavior were measured using similar protocols as in references [4,11]. In the ZFC