Superparamagnetic Behavior of $La_{1-x}Sr_xMnO_3$ Nanoparticles in the MCM-41 Molecular Sieve

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Abstract

$La_{1-x}Sr_xMnO_3$ nanoparticles were prepared by calcination of a molecular sieve MCM-41 soaked in precursor solution. Magnetic properties have been investigated by the magnetization measurements. Superparamagnetic behavior of the nanoparticles is observed both for the antiferromagnetic and ferromagnetic phases at low temperatures. For the antiferromagnetic phase, the superparamagnetic moment corresponds to the uncompensated moments in the antiferromagnetic particles. While for the superparamagnetism for the ferromagnetic phase is smaller than the superparamagnetism estimated for the single-domain ferromagnetic particles.

Key words: nanoparticle; superparamagnet; $La_{1-x}Sr_xMnO_3$; MCM-41

1. Introduction

Macroscopic quantum tunneling of magnetization has been extensively investigated from both experimental and theoretical aspects. It has been studied experimentally not only using the molecular-magnets such as Mn_{12} acetate [1], but also using the antiferromagnetic nanoparticles such as the horse spleen ferritin [2]. Recently, Takada *et al* [3] prepared Co_3O_4 nanocrystals about 3nm in diameter dispersed in the MCM-41 molecular sieve and found that the nanocrystal is a new and ideal material for the study of macroscopic magnetic quantum effects. In the present work, we have prepared $La_{1-x}Sr_xMnO_3$ (hereafter, LSMO) nanoparticles in MCM-41 and have studied its magnetic properties in order to investigate the superparamagnetizm of both the antiferromagnetic and ferromagnetic phases.

2. Experiment

The MCM-41 molecular sieve [4] with the pore about 3nm in diameter was used as a template for the fabrication of LSMO nanoparticles. An inclusion of LSMO precursor in the pores of MCM-41 is accomplished by soaking the molecular sieve in an aqueous solution of $La(CH_3COO)_3 1.5H_2O$, $Mn(NO_3)_2 6H_2O$ and $SrCl_2 6H_2O$, and the soaked sample was dried and then calcinated in flowing oxygen at 300 for 3h. We prepared two samples: the Sr content, x is 0.05 and 0.15. The bulk sample for x=0.05 shows the spin-canted antiferromagnetic phase and that for x=0.15 shows the ferromagnetic insulator phase [5]. The magnetization measurements of the samples were done using a SQUID magnetometer (Quantum Design MPMS-5S). The synchrotron-radiation X-ray diffraction for the samples was carried out using the beamline BL-1B at the PF, KEK.

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3. Results and discussion

The LSMO nanocrystals in MCM-41 show no X-ray diffraction peaks corresponding to the diffraction peaks of bulk samples, which suggests that the nanocrystals no longer preserve translational symmetry in both intra- and interpores of MCM-41, and also that there is no LSMO particles on the outside surface of the sample. The ultraviolet-visible optical absorption measurement has been performed on the nanocrystals and bulk LSMO samples. The result suggests that the LSMO nanocrystals are in MCM-41. First, we measure the temperature dependence of magnetization for the LSMO nanocrystals in MCM-41 in the field of 1kOe. For the nanocrystals of x=0.05, the magnetization has a shoulder around 100K corresponding to the antiferromagnetic ordering, and shows paramagnetic divergence at low temperatures. Such paramagnetic behavior is not observed in the bulk sample. For the nanocrystals of x=0.15, the magnetization shows ferromagnetic behavior below about 250K, though it still increases with decreasing temperature. Figure 2 shows the magnetization curves at 5K. The curve for x=0.05 shows paramagnetic behavior, on the other hand, that for x=0.15 shows ferromagnetic one. We try to fit the magnetization data to the Langevin paramagnetic function. Solid lines in Fig.2 are the Langevin function with the numbers of Mn^{+3} spins $n \approx 9$ for x=0.05 and $n \approx 28$ for x=0.15, respectively. For the antiferromagnetic nanoparticles, the number of uncompensated spins can be estimated to be the cube root of total spins in a particle. The number $n \approx 9$ is well explained by the superparamagnet moments due to the uncompensated moments of the antiferromagnet particles with a diameter of about 3 nm. However, the superparamagnetic moment corresponding to $n \approx 28$ for x=0.15 is much smaller than the moment of the single-domain ferromagnet with the same diameter. Fang and Terakura [6] calculated a surface phase diagram of LSMO as a function of x. They found that the surface magnetism is quite different from the bulk one and has a strong tendency toward the antiferromagnetic state. The small superparamagnetic moment of the nanocrystals for x=0.15 supports their calculation results.

4. Summary

We prepared LSMO nanocrystals for x=0.05 and 0.15 in MCM-41. Both the antiferromagnetic particles (x=0.05) and the ferromagnetic ones (x=0.15) show superparamagnetism. The superparamagnetic moment of the nanocrystals is reduced for the ferromagnetic nanoparticles, for which the plausible interpretation is the occurrence of the surface antiferromagtic state.

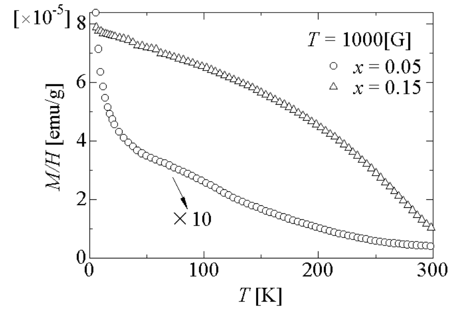

Fig. 1. The temperature dependence of magnetizations for LSMO nanocrystals in MCM-41. For the sample with x=0.05 the results are multiplied by 10.

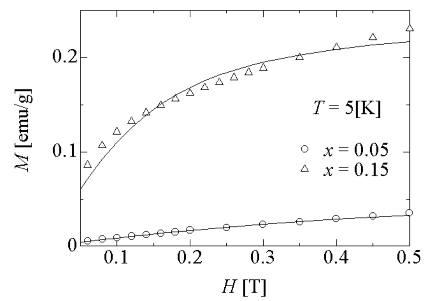

Fig. 2. Magnetizations curves for LSMO nanocrystals in MCM-41. Solid lines are best fit to Langevin functions.

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