Dilution effect on magnetic properties of Co_3O_4 nanocrystals

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We have prepared diluted systems of Co_3O_4 nanocrystals dispersed in an amorphous silicate by calcination of molecular sieve soaked in precursor solutions with concentrations of 0.01 and 0.1 mol/l. For both systems we have observed the disappearance of the antiferromagnetic phase transition at 33 K of bulk Co_3O_4, a difference in the dc susceptibility between field cooling and zero field cooling, and the frequency dependence of the ac susceptibility. Nonlinear susceptibility measurements demonstrated that the systems from the solution of 0.01 and 0.1 mol/l were in superparamagnetic and spin glass phases, respectively. The 0.01 mol/l solution system showed no peaks at any temperature, although the peak temperature for the 0.1 mol/l solution system was 18–22 K. The interparticle interactions were independent and collective for the systems from 0.01 and 0.1 mol/l solutions, respectively. © *2000 American Institute of Physics.* [S0021-8979(00)08517-0]

I. INTRODUCTION

Magnetic spin–spin interactions in diluted systems are of great interest in science and technology.[1] Nano-sized spin clusters of magnetic materials are expected to show superparamagnetic or spin glass behavior, depending on the concentration of the systems, and to lead a development of high-density memory devices. The intercluster interaction should vary with the magnetic dipole concentration of the system since classical long-range ordering cannot be achieved in the diluted systems. An assembly of noninteracting spin clusters should represent the superparamagnetism. Collective interaction of spin clusters should result in the spin glass state.

It is well known that Co_3O_4 has a normal spinel structure and bulk Co_3O_4 exhibits antiferromagnetism with the Néel temperature at around 30 K.[2] The Co^{3+} ($3d^6$) ions at the octahedral sites are diamagnetic in the octahedral crystal field. The Co^{2+} ions at the tetrahedral sites form an antiferromagnetic sublattice with the diamond structure below the Néel temperature. On the contrary, the diluted systems of Co_3O_4 nanocrystals are expected to show a superparamagnetic or spin glass behavior depending on the concentration of the system. The magnetic frustration refers to competition between different terms in the Heisenberg exchange Hamiltonian [$H_{ex}=-\Sigma_{i,j}J_{i,j}(S_i\cdot S_j)$] so that no spin configuration simultaneously minimizes each term, where $J_{i,j}$ is the effective exchange integral between clusters i and j having total spins S_i and S_j. The spin glass behavior is a consequence of collective magnetic dipole–dipole interaction.

In this paper we report that diluted systems of Co_3O_4 nanocrystals dispersed in nonmagnetic silicate from the precursor solutions of 0.01 and 0.1 mol/l were in superparamagnetic and spin glass states, respectively. The interactions of spin clusters were independent and collective for the lower and higher concentration systems, respectively.

II. EXPERIMENT

The MCM-41 molecular sieve[3] was used as a template for fabrication of the diluted systems of Co_3O_4 nanocrystals. The molecular sieve was synthesized from a mixture of amorphous SiO_2 1.00: $C_{12}H_{25}N(CH_3)_3Cl$ 0.70: NaOH 0.24: H_2O 53.7 in molar ratio. The mixture was stirred at room temperature and then heated at 140 °C for 48 h. After thermal dehydration the dried mixture was calcinated at 700 °C for 6 h in flowing oxygen. The molecular sieve was soaked in $CoCl_2$ aqueous solutions with the concentrations of 0.01 and 0.1 mol/l. These soaked samples were dried and then calcinated in flowing oxygen at 750 °C for 3 h. The samples with the 0.01 and 0.1 mol/l $CoCl_2$ solutions contained about 1 and 6 mol % Co_3O_4, respectively. The Co_3O_4 powders used as a reference were obtained from the 0.01 mol/l solution by the same process without the molecular sieve.

X-ray diffraction (XD) patterns of the samples were measured with a Rigaku CN2013 diffractometer using Cu$K\alpha$ radiation. The size of Co_3O_4 crystalline samples were determined from the full width at half maximum of the (311) reflection using Scherrer's equation.[4] Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design MPMS 5S).

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the x-ray diffraction pattern of the molecular sieve sample (a) can be indexed on a hexagonal unit cell with $a\sim4.0$ nm ($a=2d_{100}/\sqrt{3}$ and $d_{100}=3.2$ nm).

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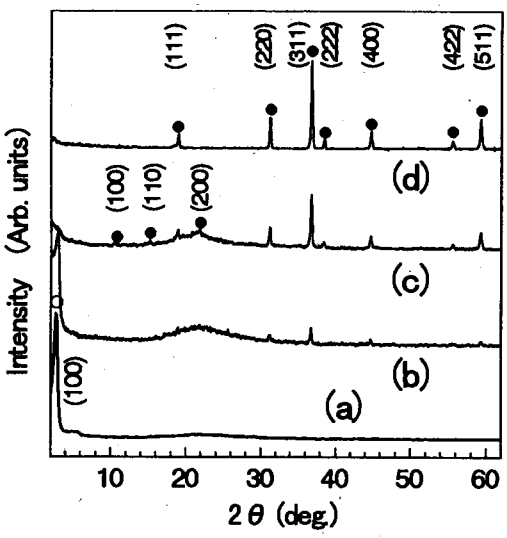

FIG. 1. X-ray diffraction patterns with Cu$K\alpha$ radiation of the molecular sieve (a), the Co_3O_4 diluted systems from the 0.01 mol/l solution (b) and from the 0.1 mol/l solution (c), and the Co_3O_4 powders (d). ●:Co_3O_4 and ○:MCM-41 molecular sieve.

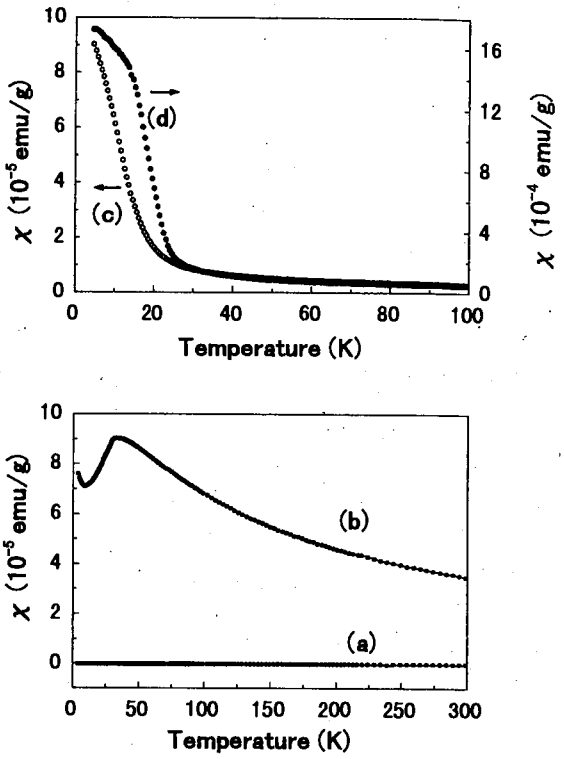

FIG. 2. Temperature dependent dc magnetic susceptibilities in $H=1000$ G of the molecular sieve (a) and the Co_3O_4 powders (b) in the lower panel, and those of the Co_3O_4 diluted systems from the 0.01 mol/l solution (c) and the 0.1 mol/l solution (d) in the upper panel.

The samples of Co_3O_4 nanocrystals in amorphous silicate can be fabricated by the soaking and calcination process shown by the x-ray diffraction patterns of Fig. 1(b) and (c). The x-ray diffraction pattern Fig. 1(d) represents the Co_3O_4 powders obtained from the 0.01 mol/l solution. The crystalline sizes of the Co_3O_4 nanocrystals from the 0.01 and 0.1 mol/l solutions and that of the powders from the 0.01 mol/l solution were 15, 16, and 19 nm, respectively. The crystalline sizes of the samples were almost the same. We have succeeded in preparing the diluted systems of Co_3O_4 nanocrystals in the silicate.

As shown in Fig. 2 (lower panel), the molecular sieve sample (a) was nonmagnetic, although Co_3O_4 powder sample (b) showed antiferromagnetism with the Néel temperature at about 33 K. In the diluted systems of Co_3O_4 nanocrystals the antiferromagnetic phase transition disappeared, and the systems showed ferrimagnetic behavior below 30 K as shown in Fig. 2 (upper panel). For the diluted systems the temperature dependence of magnetic susceptibility differed from each other. The system from the 0.01 mol/l solution (c) showed lower ferrimagnetic onset than that from the 0.1 mol/l solution (d). Curie–Weiss behavior was also observed in the temperature region from 100 to 300 K for the diluted systems. In the diluted systems magnetic Co_3O_4 are surrounded by nonmagnetic silicate. The higher density of Co_3O_4 nanocrystals brought about stronger interaction between the spin clusters. The disappearance of antiferromagnetic transition suggests that the degree of randomness is not as small for the diluted systems. In the diluted systems, the randomness may induce local canted states when the relative dipole orientations are frozen in a metastable state, and it leads to an independent superparamagnetic or collective spin glass behavior depending on the spin cluster density.

In order to demonstrate the dilution effect on magnetic interaction, we have measured the dc magnetization of the diluted systems below 100 K in a magnetic field of $H=1000$ G after zero field cooling and field cooling. As shown in the inset of Fig. 3 (lower panel), we have observed a cooling history dependence of the susceptibility for the diluted system from the 0.01 mol/l solution. An apparent discrepancy between the field cooled and zero field cooled susceptibilities below 15 K was observed for the system from the 0.1 mol/l solution, as seen in Fig. 3 (upper panel). A sharp maximum in the zero field cooled susceptibility appeared at around 10 K for the diluted system from the 0.1 mol/l solution is an implication of interacting spin clusters. The zero field cooled susceptibility is expected to indicate a maximum at the freezing temperature. The higher density must bring about the higher freezing temperature in the spin clusters assembly.

At the freezing temperature in a finite field magnetic dipoles cannot follow the ac external field, therefore the imaginary part appears in the ac susceptibility. The ac susceptibility of the samples measured in $H=2$ G and at the frequency of $f=100$ Hz below 100 K are shown in Figs. 4 and 5. The real (χ') and imaginary (χ'') parts of the ac susceptibility (linear components) were clearly observed. The temperature dependencies of χ' and χ'' were consistent with each other. The cusp temperature of the χ' curve was located at nearly the same temperature as the inflection point of the χ'' curve. For the diluted system from the 0.01 mol/l solution a cusp of the χ' was at 8 K as shown in Fig. 4. The frequency dependence of the real part χ' of the ac susceptibility for the system from the 0.01 mol/l solution measured from $f=1$ to 1000 Hz in $H=230$ G is shown in the inset of Fig. 4. χ' showed a broad maximum at around 8 K. The maximum point shifted to a higher temperature as the frequency in-

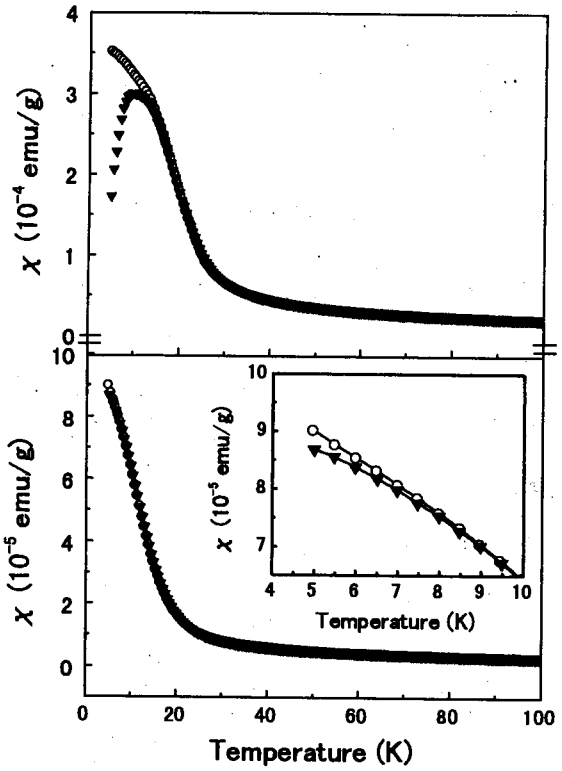

FIG. 3. Temperature dependencies of the field cooled (○) and zero field cooled (▼) susceptibility in $H=1000$ G of the Co_3O_4 diluted systems from the 0.01 mol/l solution (lower panel) and from the 0.1 mol/l solution (upper panel).

creased. The system from the 0.1 mol/l solution also indicated the χ' and χ'' of the ac susceptibility, and we have observed two components showing cusps at 17 and 21 K in the χ' as shown in Fig. 5. The inset of Fig. 5 shows the frequency dependence of the χ' for the system from the 0.1 mol/l solution measured from $f=1$ to 1000 Hz in $H=230$ G. The broad maximum at around 15 K of the χ'

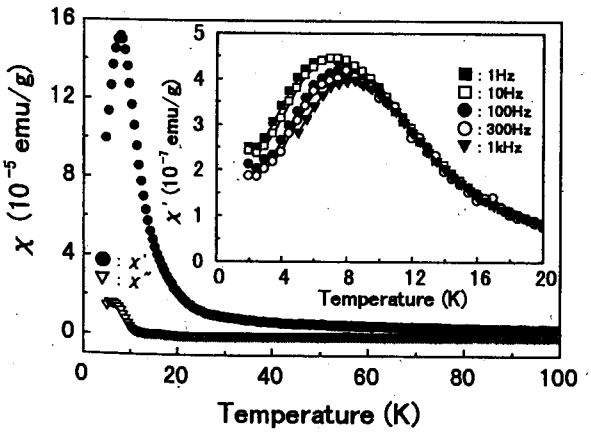

FIG. 4. Temperature dependence of ac susceptibility, χ' and χ'', in $H=2$ G and at $f=100$ Hz of the Co_3O_4 diluted system from the 0.01 mol/l solution. Inset: Frequency dependence of the real part of ac susceptibility χ' from $f=1$ to 1000 Hz in $H=230$ G of the Co_3O_4 diluted system from the 0.01 mol/l solution.

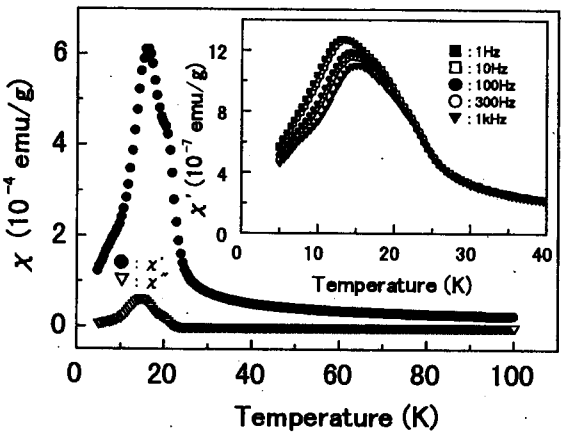

FIG. 5. Temperature dependence of ac susceptibility, χ' and χ'', in $H=2$ G and at $f=100$ Hz of the Co_3O_4 diluted system from the 0.1 mol/l solution. Inset: Frequency dependence of the real part of ac susceptibility χ' from $f=1$ to 1000 Hz in $H=230$ G of the Co_3O_4 diluted system from the 0.1 mol/l solution.

shifted to higher temperature as the frequency increased. Frequency dependence can be understood as an indication of a superparamagnetic or spin glass material.[5]

It is well known that a spin glass phase can be specified by the nonlinear susceptibility χ_3. The magnetization m is expressed as

$$m=\chi_1 h+\chi_3 h^3+\chi_5 h^5+\cdots,$$

when the applied ac field $h=h_0 \sin(\omega t)$ is so small. Here, χ_1 is the linear susceptibility, and χ_3 and χ_5 are the nonlinear susceptibilities. The 3ω component can be given by

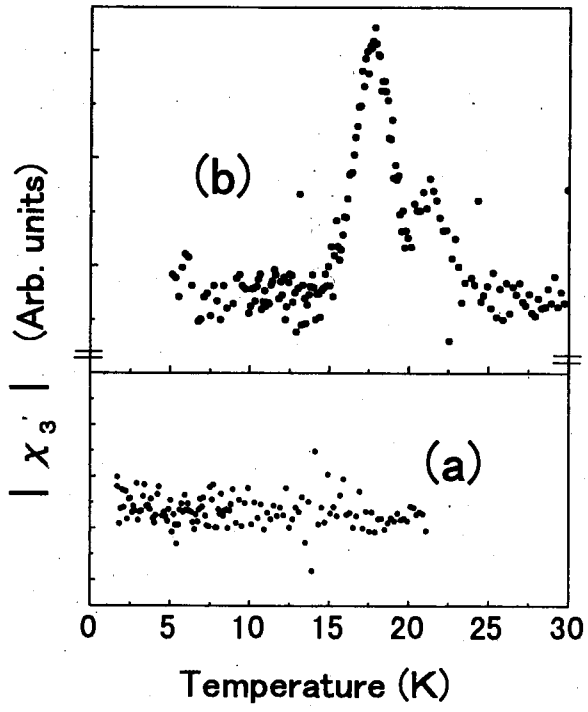

FIG. 6. Temperature dependence of nonlinear susceptibility χ_3' (3ω signal) at $f=0.1$ Hz with $h_0=2$ G of the diluted systems from the 0.01 mol/l solution in 1.7–20 K (a) and from the 0.1 mol/l solution in 5–30 K (b).

$$M_{3\omega}=-(1/4)\chi_3 h_0^3-(5/16)\chi_5 h_0^5-(21/64)\chi_7 h_0^7+\cdots.$$

Therefore, the real part χ_3' is given as $\chi_3'=-4M_{3\omega}'/h_0^3$, and is proportional to higher harmonic signals of frequency 3ω. The temperature dependence of the nonlinear susceptibility χ_3' of the diluted systems from the 0.01 and 0.1 mol/l solutions were measured at $f=0.1$ Hz with $h_0=2$ G in the temperature ranges 1.7–20 K and 5–30 K, respectively. The system from the 0.01 mol/l solution showed no peaks below 20 K as shown in Fig. 6(a), whereas the system from 0.1 mol/l solution showed two divergent peaks at 18 and 22 K as shown in Fig. 6(b). The nonlinear susceptibility measurements revealed that the systems from the 0.01 and 0.1 mol/l solutions were in superparamagnetic and spin glass phases, respectively. The 0.01 mol/l solution system showed no peaks at any temperature, although the peak temperature for the 0.1 mol/l solution system was 18–22 K. The double peaks in the nonlinear susceptibility may reflect nonuniform distribution of the distance between Co_3O_4 nanocrystals in the samples. The independent and collective magnetic interactions between spin clusters reflect the concentrations of the Co_3O_4 nanocrystals dispersed in nonmagnetic silicate.

IV. SUMMARY

We have prepared the diluted systems of Co_3O_4 nanocrystals dispersed in an amorphous silicate by calcination of molecular sieve soaked in precursor solutions with the concentrations of 0.01 and 0.1 mol/l. The antiferromagnetic phase transition at 33 K of bulk Co_3O_4 disappeared, and the behaviors of superparamagnetism and spin glass were observed for the systems with lower and higher precursor concentrations, respectively. The collective intercluster interactions were smaller for the system from the 0.01 mol/l solution than that from the 0.1 mol/l solution. The short-range interaction between spin clusters dominated the magnetic property of the diluted Co_3O_4 nanocrystals.

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