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Preparation and Magnetic Properties of CoCrFeO$_4$ Nanocrystals

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Magnetic nanoparticles are of great current interest, both from a fundamental point of view and for applications in materials science.[1,2] Below a critical size, magnetic particles become single-domain and exhibit unique phenomena such as superparamagnetism, quantum tunneling of the magnetization, and unusually large coercivities.[3-5] Knowledge of these fundamental

properties is essential for creative use of nanoparticles in important technical applications. In the past decade, many investigations have been performed on the nanoparticles of metals such as Fe, Co, and Ni.[6-8] However, the nanoparticles of metal oxides are more stable and allow for a relative tunability of the magnetic properties, thus demonstrating great potentials for applications. For these reasons, the magnetic properties of ferrite nanocrystals (MnFe$_2$O$_4$,[9] MgFe$_2$O$_4$,[10] CoFe$_2$O$_4$,[11,12] NiFe$_2$O$_4$,[13,14] and ZnFe$_2$O$_4$[15,16]) are attracting more interest.

In this work, a spinel compound, CoCrFeO$_4$, was synthesized on the nanoscale. We report here an investigation of the magnetic properties of this compound.

CoCrFeO$_4$ nanocrystals were prepared through a stearic sol−gel method. First, stearic acid (50 g) was dissolved in 100 mL of deionized water, and then cobalt acetate (24.9 g), chromium acetate (40.0 g), and ferric nitrate (40.4 g) were added. After mixing was complete, the solution was heated to 80−100 °C for 2h, and a homogeneous transparent sol was obtained. The sol was slowly cooled to ambient temperature, forming a gel.

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Table 1. Results of Element Analysis

	Co (wt %)	Cr (wt %)	Fe (wt %)
observed	35.9	30.9	33.2
calculated	35.3	31.2	33.5
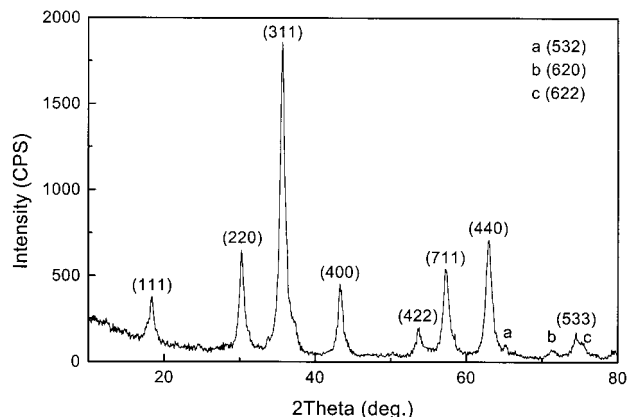
Figure 1. X-ray diffraction pattern of the final product.
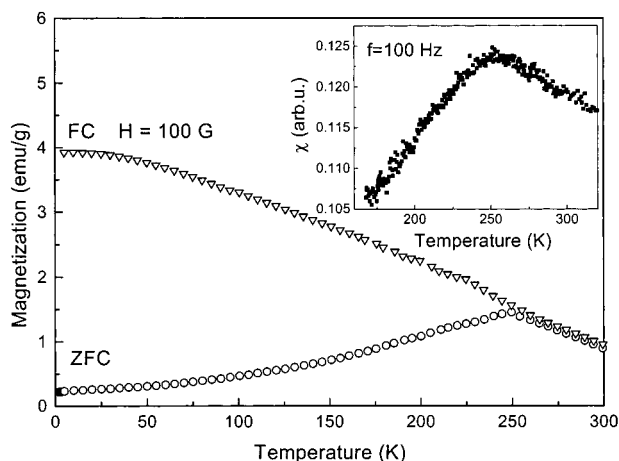
Figure 2. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization of CoCrFeO$_4$ nanocrystals under a magnetic field of 100 G. Inset: Temperature dependence of the ac magnetization susceptibility.

Finally, the gel precursor was heat-treated at 500 °C to obtain loose black powders.

Chemical analysis was performed with an inductively coupled plasma emission spectrometer (ICP). The results showed excellent agreement between the expected and observed values of the constituent elements in the product (Table 1).

Figure 1 shows the X-ray diffraction (XRD) pattern of the powder sample. The pattern can be suitably indexed on a cubic structure with the space group O_h^7-($Fd3m$), and no impurity peak can be observed. The transmission electron microscopy image shows that the particles have spherical shapes. The distribution fits well to a log−normal distribution with a narrow width of $\sigma = 0.23$ and a mean size of $D_0 = 8.1$ nm.

Magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (MPMS-5). The curves of the zero-field-cooled (ZFC) and field-cooled (FC) measurements are shown in Figure 2. The ZFC magnetization increases as the temperature rises from 5 K. When the temperature approaches 249 K, the magnetization reaches a maximum and starts to decrease. The FC magnetization

shows its maximum at 5 K and steadily decreases as the temperature increases. Starting at around 249 K, the magnetizations from the ZFC and FC measurements overlap with each other. This observation is consistent with the behavior of ultrafine magnetic particles, which are known to mimic some of the properties of spin-glass materials and to exhibit blocking temperatures.[17] As the temperature decreases in the ZFC process, the potential energy settles to a minimum by aligning the magnetization of each nanoparticle along its easy axis. Because of the random packing of the nanoparticles, the magnetization of the sample has its lowest value at 5 K. When the temperature rises under an applied magnetic field, energy barriers start to be overcome, and superparamagnetic relaxation occurs. The overall magnetization increases with increasing temperature, and the maximum magnetization is achieved at T_B. When all of the nanoparticles are at the superparamagnetic relaxation state above T_B, their magnetization follows the Curie law, decreasing with increasing temperature. However, in the FC process, the magnetization direction of all of the nanoparticles is frozen in the field direction. The magnetization exhibits a maximum at 5 K. Above T_B, all of the nanoparticles are at the superparamagnetic relaxation state, as is the case in the ZFC process. As a result, the magnetization measurements in the ZFC and FC processes give overlapping data. The dynamics of the particle assemblies was also studied by ac magnetic susceptibility measurements, and the results are shown in the inset of Figure 2. The blocking temperatures determined from the peak of the dc magnetization and the ac magnetic susceptibility are slightly different (by approximately 1 K), specifically, the T_B value determined from the ZFC process is slightly lower than that determined from the FC process. As we know, the blocking temperature represents the temperature at which the superparamagnetic relaxation time is comparable to the time scale of the measurement, so the above difference might be due to the different time scales of these two measurements. High-temperature magnetic susceptibility measurements demonstrate that the Curie transition temperature of CoCrFeO$_4$ nanocrystals is around 780 K.

CoCrFeO$_4$ nanoparticles show hysteresis behaviors for their field-dependent magnetization below the blocking temperature (249 K). Figure 3 shows the hysteresis loops of the nanoparticles at different temperatures. The coercivity H_C of the nanoparticles increases with decreasing temperature (inset of Figure 3). According to the Stoner−Wohlfarth theory, the H_C value for a single-domain particle is

$$H_C = \frac{2K}{\mu_0 M_S} \qquad (1)$$

where μ_0 is a universal constant of permeability in free space and M_S is the saturation magnetization of the nanoparticle. Below the blocking temperature, M_S slowly increases with decreasing temperature. Nevertheless, K increases faster than M_S, and H_C increases with decreasing temperature as indicated by eq 1. This is consistent with our experiment results. However, a

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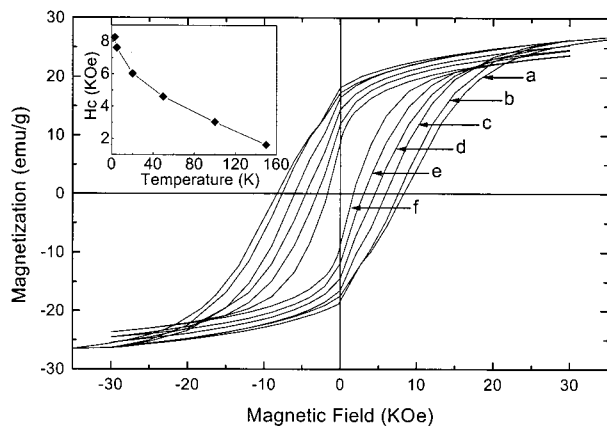
Figure 3. Magnetization versus applied magnetic field for $CoCrFeO_4$ nanocrystals at different temperatures: (a) 3, (b) 5, (c) 20, (d) 50, (e) 100, and (f) 150 K. Inset: Correlation between coercivity and temperature.

careful analysis of the $H_C - T$ curve clearly reveals that a strong increase in H_C occurs below 50 K. A similar increase of the coercivity was found by B. Martinez et al. for γ-Fe_2O_3 nanoparticles[18] and could be attributed to the extra energy required to switch the spins that were pinned by exchange interactions with the frozen spin-glass surface layer.

The saturation magnetization M_S was determined by $H^{-1} \rightarrow 0$ extrapolation. The results are shown in Figure 4. In general, for temperatures below the Curie temperature, the magnetization temperature dependence was described by Bloch, who found that

$$M(T) = M(0)(1 - BT^b) \qquad (2)$$

where $M(T)$ is the temperature-dependent magnetization, B is the Bloch constant, and b is the Bloch exponent. The exponent is given by $b = {}^3/_2$ for a bulk system and has been well verified. For the nanoscale system, Hendriksen et al. considered the spin-wave spectrum of particles by solving the Heisenberg Hamil-
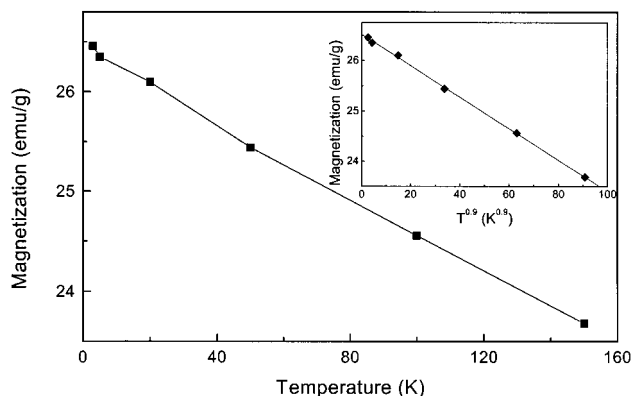

Figure 4. Saturation magnetization versus temperature for $CoCrFeO_4$ nanocrystals. Inset: Results of linear fits of Bloch's law to the data with the Bloch exponent $b = 0.9$.

tonian and found that the excitations were a function of radial position in the particles. The qualitative theoretical expectation for this result is that reduced coordination at the surface will cause the spins to be more susceptible to thermal excitation, which leads to larger magnetization temperature dependencies.[19] However, experimental investigations of $M(T)$ for nanoparticles are a matter of controversy. A measurement on Fe−C particles with a diameter of 3.1 nm found $b = 1.9$.[20] For $MnFe_2O_4$ nanoparticles prepared by a coprecipitation reaction, b was determined to lie in the range 1.5−1.9 for sizes in the range 5−15 nm.[9] In our present work, linear fitting of eq 2 to the data of Figure 4 led to the value $b = 0.9$ (inset of Figure 4). Recently, D. Zhang et al. also found for Fe nanoparticles that, with decreasing size, the Bloch exponent fell from ${}^3/_2$ to smaller values.[21] To understand the results, in addition to reduced coordination, namely, size effects, the nature of the coordination might also be important. Both the size and the interface of nanoparticles have a great influence on their magnetic properties. Further investigations are in progress to unravel these dependencies.

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