

Temperature Dependence of Morphology and Magnetic Properties of Cobalt Nanoparticles Prepared by an Inverse Micelle Technique

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We have fabricated cobalt nanoparticles using sodium borohydride reduction of cobalt chloride in a didodecyltrimethylammonium bromide (DDAB)/toluene inverse micelle solution. The particle morphology changed from single particles to clusters as we increased the reaction temperature. Intracuster dipole–dipole interaction increased the blocking temperature and reduced the effective magnetic moment per cluster.

1. Introduction

Particles and clusters with length scales from 1 to 100 nm have novel electrical, chemical, and magnetic properties, compared with their corresponding bulk materials.^{1,2} These new properties are likely due to the quantum confinement of electrical charge carriers and the increasing predomination of low-coordination-symmetry surface atoms as the particle size decreases.^{3,4}

Among various kinds of nanoparticles made from different materials, magnetic nanoparticles of 3D transition metals have attracted a great deal of attention recently for several reasons.⁵ First, from the fundamental point of view, 3D transition metal nanoparticles provide a direct link between atomic level magnetism and bulk magnetism. Second, they have potential applications in magnetic information storage,⁶ color imaging, and magnetic refrigeration.⁷

During the past decade, many different methods have been developed to synthesize nanoparticles and clusters. Bloomfield et al.^{8,9} and de Heer et al.¹⁰ produced Co, Ni,

and Fe clusters of 40–500 atoms by laser vaporization (gas-phase method) and studied those clusters using a Stern–Gerlach apparatus. Clusters made with this technique are usually “naked”, which means that their surfaces are not coated by other molecules. Magnetic measurement on those “naked” clusters showed that the moments of these clusters are significantly enhanced compared with the bulk value. A widely accepted explanation of these discoveries is based on the fact that the surface atoms of the nanosized particle have a lower coordination number and the spin moment is much higher than that for atoms in the bulk.¹¹ However, it still remains an open question whether the unquenched orbital moment on the surface plays a role in this enhancement. Chemical methods, including the Rieke method,^{12,13} the inverse micelle technique,^{14–16} and most recently the sonochemical method,¹⁷ provide alternative ways to synthesize nanoparticles. Compared with the gas-phase methods, chemical methods can provide larger amounts of final product using a relatively simple apparatus, which is crucial for industrial applications. Particles made from chemical reaction are usually coated with other molecules in order to prevent them from aggregation and possible oxidation from the air. The physical and chemical properties of these coated

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nanoparticles are very different from the "naked" nanoparticles prepared from the gas-phase method.¹⁸

Our group has used the inverse micelle technique to produce cobalt nanoparticles.¹⁵ Inverse micelles are nanometer sized cages formed by dissolving surfactant molecules in an apolar organic solvent. The hydrophilic ends of the surfactant molecules will spontaneously gather together to form a cavity with hydrophobic ends sticking out into the solvent. The size of this cage usually can be varied by the amount of water contained inside the cage. Various chemical reactions can be carried out inside the micelle cage to synthesize nanoparticles. The growth of the particle is hindered by the surfactant molecules. Particles formed by this method are usually well dispersed in the colloid due to the surface coating of surfactant molecules. We have used NaBH₄ to reduce CoCl₂·6H₂O in the micelle solution. Our previous studies¹⁵ showed that we could form nanometer Co particles inside the micelle with a fairly uniform size distribution. In this paper, we show that the morphology of the final product in this synthesis depends largely on the reaction temperature. At low reaction temperature, isolated single particles were obtained, while clusters with a finite number of monomers were formed at high reaction temperature. We also show that the magnetic properties are dependent on the clustering due to dipolar interactions which increase the magnetic anisotropy energy barrier, leading to changes in the blocking temperature, the magnetic moment, and other related magnetic properties in the cluster system. In section 2, we will present our synthesis procedures, and in section 3, some experimental results of our system will be discussed.

2. Experimental Section

The surfactant didodecyltrimethylammonium bromide (DDAB) (98%) was purchased from Fluka and used as received. The solvent toluene was obtained from Fisher and further purified by distillation. CoCl₂·6H₂O (98%) and NaBH₄ (99%) were purchased from Aldrich and used as received. All the synthesis steps were carried out in an Ar environment to avoid possible oxygen contamination during the reaction. Toluene and deionized water were bubbled with Ar gas for 2 h before the experiment to remove oxygen. DDAB (1.5 g) was dissolved in 10.4 mL of toluene solution using a 25 mL flask to form a 0.3 M micelle solution. CoCl₂·6H₂O (23.98 mg) was then added to 10 mL of the clear micelle solution. The mixture was sonicated until all the solid disappeared and a clear blue solution was obtained. The desired reaction temperature of the micelle solution was obtained using a home-made temperature control unit. NaBH₄ (113 mg) was dissolved in 3 mL of deionized water to yield a 1 M solution using a separate beaker. The 1 M NaBH₄ solution (300 μ L) was slowly added to the micelle solution using a Hamilton microsyringe while vigorously stirring the solution with a magnetic stirring bar. Depending on the reaction temperature, a stable black colloid would appear after 1–2 min. The reaction mixture was stirred for another 10–15 min to ensure a complete reaction. One drop of colloid was diluted with excess toluene in a small capped vial. A drop of the diluted colloid was later put on a carbon-coated copper grid for transmission electron microscopy (TEM) examination. All the TEM images were obtained with a Philips EM201 electron microscope. Electron diffraction was done on a Philips CM12 microscope. After toluene was evaporated from the colloid under an Ar environment for 2 days, a powder sample was obtained. The magnetic properties of this powder sample were measured using a Quantum Design MPMS SQUID magnetometer. Alternatively, the powder sample was washed with excess acetone. A black precipitate was isolated from the washing solution. A small amount of the precipitate was collected and sonicated in toluene for TEM examination.

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3. Results

Particles were synthesized at different reaction temperatures. Figures 1 and 2 shows the TEM images and corresponding histograms of particles synthesized at 13, 22, 33, and 41 °C. Monodispersed single particles were obtained at low reaction temperature (13 °C). The average diameter of the particles was about 44 Å. The particle size increased to about 57 Å, as the reaction temperature increased to 22 °C. Further increase of the reaction temperature caused the particles to aggregate. At around 41 °C, small clusters with a finite number of monomers (ca. 5) became the major component. The monomer diameter is approximately equal to 44 Å.

We propose that this morphology difference is due to the change of interaction between micelles at different temperatures. At low temperature, isolated single particles are obtained because the repulsive force between hydrophobic surfactant molecules coated on different particles can prevent them from aggregation. As the temperature increases, surfactant layer flexibility increases and therefore allows interpenetration of the surfactant hydrophobic tails of different particles or even possibly the formation of dumbbell-shaped micelles.¹⁹ Experimentally, it has been found that a short range attractive interaction exists due to the overlapping of surfactant hydrocarbon tails at a relatively high temperature.²⁰ We believe that this short range attraction force is the mechanism for forming cobalt clusters at high reaction temperature.

We also found that clusters formed at the high reaction temperature were very easy to coalesce under a high-intensity electron beam. Figure 3 shows the same portion of clusters before and after an increase of the electron beam intensity. The same coalescence process occurred if clusters stayed under a weaker electron beam for a longer time. Clusters formed at 41 °C coalesced into 76 Å diameter spherical particles. Considering that monomer size is around 44 Å, a simple calculation shows that the average number of monomers in each cluster is around 5.1, corresponding well to the direct TEM observation. It is well-known that small clusters have their melting point depressed relative to that of the bulk.²¹ Even below the actual melting point, clusters tend to sinter into a spherical shape in order to minimize the surface energy. The structure change of nanoparticles under an electron beam has also been observed by other groups.²² A future experiment is needed to determine whether the coalescence we observed is a melting process or not.

One problem that exists in most surfactant-stabilized nanoparticle systems is that a large amount of excess surfactant always exists in these systems. To concentrate the final product, acetone was added to the colloid, which induced an immediate flocculation of the solution. An alternative method was to wash the dried powder sample with excess acetone. Regardless of the method we used, a black precipitate was separated from the solution using a separatory funnel. The remaining acetone washing solution was dried, and more than 90% of the surfactant was recovered, indicating that most of the excess surfactant was removed. Figure 4 shows a TEM image of the edge of the black precipitate. Compared with the cases of

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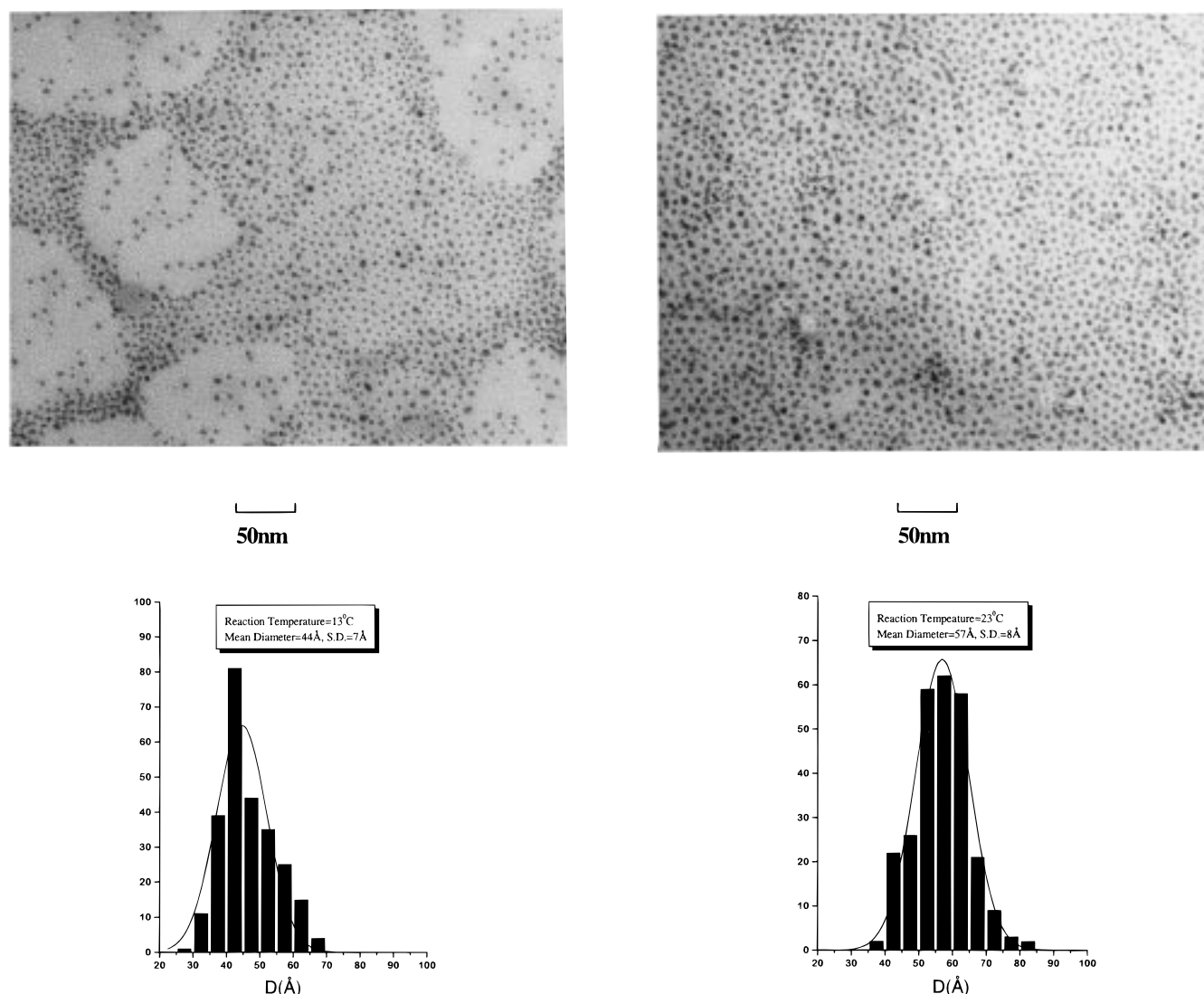


Figure 1. TEM images of particle and cluster morphology and corresponding size histograms at different reaction temperatures: (a) 13 °C; (b) 22 °C.

Figure 1 and 2, the acetone precipitated sample contains a large amount of closely packed nanoparticles. The particles are well separated from each other, indicating that they are still coated with a surfactant layer.

Our previous studies^{23,24} showed that NaBH_4 reduction of Co^{2+} ions without surfactant resulted in either Co_2B or Co metal, depending on whether the environment is aqueous or nonaqueous. The environment of Co^{2+} ions in the inverse micellar solution, however, is much more complex. Nagy et al.¹⁶ studied extensively its dependence on the nature of the surfactant and the cosurfactant, the amount of water, and the organic solvent. The final product of the reaction depends largely on the environment of the Co^{2+} ions. Selected area electron diffraction (SAED) performed on the acetone-precipitated sample confirmed that face-centered cubic (fcc) cobalt was formed inside our solution micelles.

Since the monomer size of clusters formed at the high reaction temperature is almost equal to the size of single particles formed at the low reaction temperature, these two samples provided an excellent opportunity to study

the change of magnetic properties as a result of monomer interactions within clusters.

Magnetic properties were measured using the dried colloid powder sample. The amount of cobalt contained in our sample was very small. For the acetone-precipitated sample, the loss of a small amount of the precipitate during filtration might introduce a large experimental error in the cobalt mass determination. Therefore, the directly dried powder sample was used to make magnetic measurements, since no cobalt was lost during the drying process. Furthermore, the dried powder sample was better protected from oxygen by a thick surfactant layer compared with the acetone-precipitated sample. Even so, the sample was transferred from the argon environment to the SQUID magnetometer as fast as possible to minimize the exposure time in the air.

Figure 5 shows the zero-field-cooled (ZFC) magnetization versus temperature curves for the spherical particles synthesized at 13 °C and the clusters formed at 41 °C. The sample was first cooled at zero magnetic field to 2 K, and then a 1.59×10^4 A/m magnetic field was applied and the magnetization measurement was taken with increasing temperature. A transition between the ferromagnetic state and the superparamagnetic state occurs at a temperature known as the blocking temperature (T_B). The magnetic

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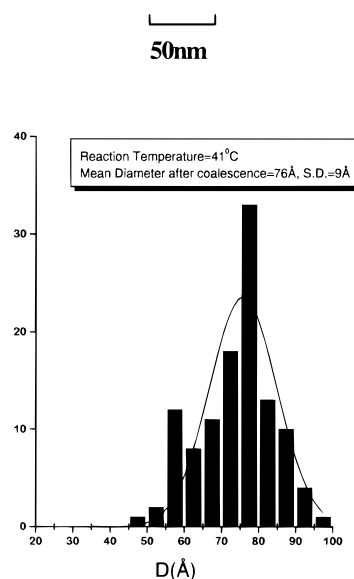
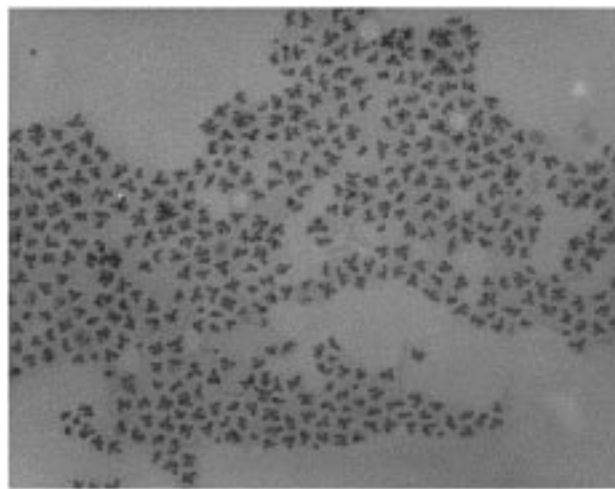
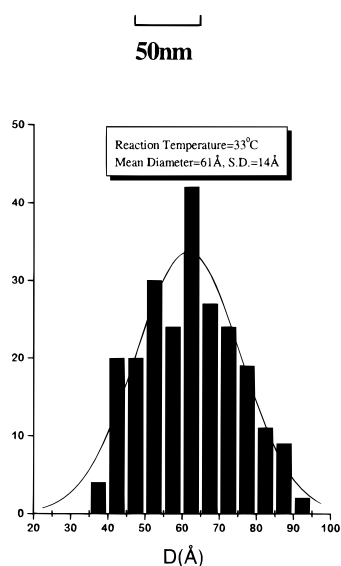
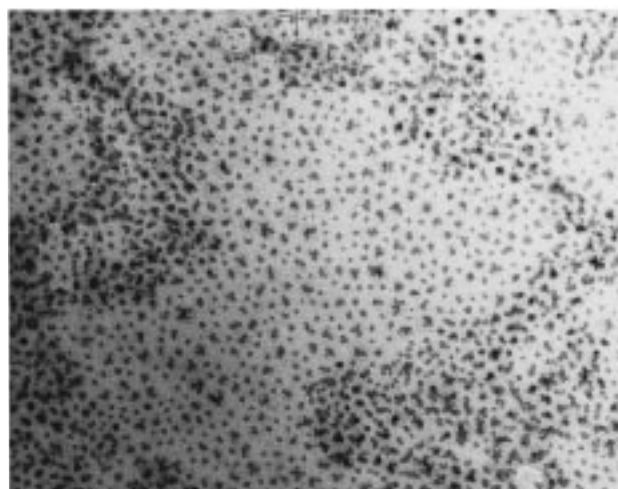


Figure 2. TEM images of particle and cluster morphology and corresponding size histograms at different reaction temperatures: (a) 33 °C; (b) 41 °C.

signal from the surfactant was subtracted from the directly measured data.

Above the blocking temperature, the thermal energy is higher than the anisotropy energy barrier and switching of the magnetization direction between energy minima can occur, a phenomenon called superparamagnetism. Therefore, above T_B , the magnetization should decrease with the temperature according to the Langevin function²⁵

$$M = M_s \left(\coth \alpha - \frac{1}{\alpha} \right) \quad (1)$$

where M_s is the saturation magnetization. The function in parentheses is the Langevin function with the parameter $\alpha = \mu_p H / k_B T$, μ_p is the average magnetic moment per particle, H is the applied magnetic field, and k_B is the Boltzmann constant. By fitting the experimental data with Langevin curves in the superparamagnetic regime, the average magnetic moment per particle or cluster can be determined. However, a simple fitting curve with a constant magnetic moment shows a slight mismatch with

the experimental data in the high-temperature regime. Including convolution of the size distribution with the Langevin function did not improve the fitting. We therefore attributed it to the fact that the magnetic moment of nanosize particles decreases with increasing temperature much faster than that of the corresponding bulk material. An empirical temperature dependent magnetic moment $\mu_p = \mu_{p0} e^{-cT}$ (constant c varies from 0.010 to 0.020) was introduced to improve the fitting (solid and dashed curves in Figure 5). We believe that this strong dependence of magnetic moment is related to the properties of surface atoms, which are quite different from their bulk counterparts. The results listed in Table 1 show that the zero temperature magnetic moment per cluster (those synthesized at 40 °C or greater) μ_{p0} is, in all cases, less than four times the magnetic moment of single particles synthesized at lower temperatures. This is smaller than expected because there are typically five or more particles per cluster and because the coalesced radius of the cluster (see Figure 2b) implies the cluster has approximately five times as much mass as the single particles. This small cluster moment indicates that the magnetic moments of monomers inside the clusters are not coupled ferromagnetically. Intracuster dipole–dipole interactions which

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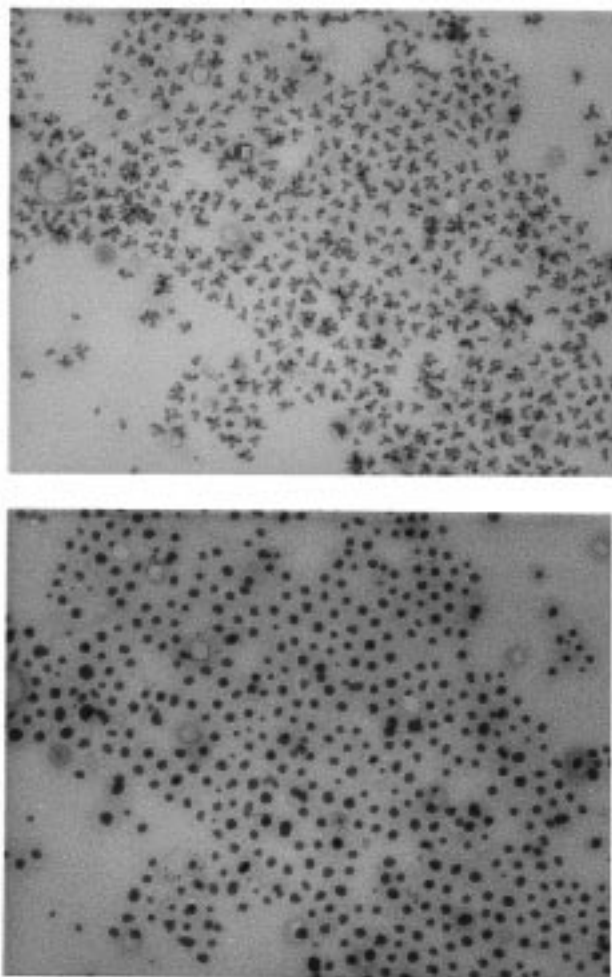


Figure 3. Coalescence of the same portion of clusters under the TEM electron beam: (a, top) under the low-intensity electron beam; (b, bottom) under the high-intensity electron beam.

favor antiferromagnetic coupling between the monomers affected the overall moment of the cluster. A simple calculation shows that the magnetic potential energy under the 1.59×10^4 A/m applied field and the dipole-dipole interaction between monomers are both around 10^{-22} J. Therefore, the applied field is not strong enough to defeat the dipolar interaction and hence completely align the particles in the cluster. Thus the effective moment per cluster is smaller than the sum of monomer moments.

According to Neel's theory of superparamagnetism,²⁶ the blocking temperature of a single domain particle is related to the particle volume (V) and the anisotropy constant (K) by

$$25k_B T_B = KV \quad (2)$$

As shown in Table 1, the anisotropy constant of the smallest particles, 44 Å, calculated from equation 2 is $(2.5-2.8) \times 10^5$ J/m³, which is an order of magnitude larger than the bulk fcc value. This enhanced anisotropy constant is due to the large surface anisotropy for nanosize particles.

Figure 6 shows the blocking temperatures of the single particles and the clusters synthesized at different temperatures. For the single particles, the blocking temper-

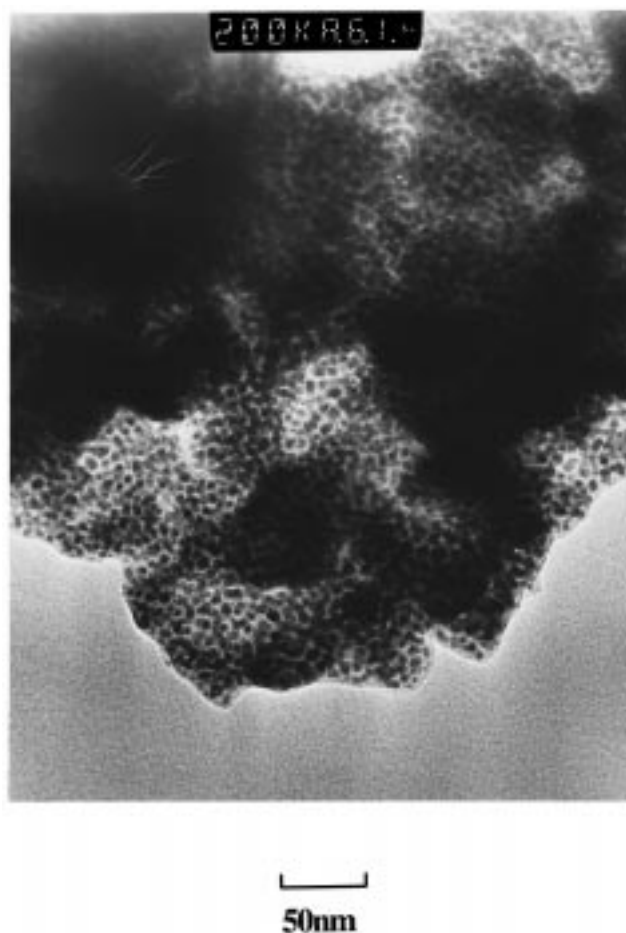


Figure 4. TEM image of closely packed Co particles after acetone extraction.

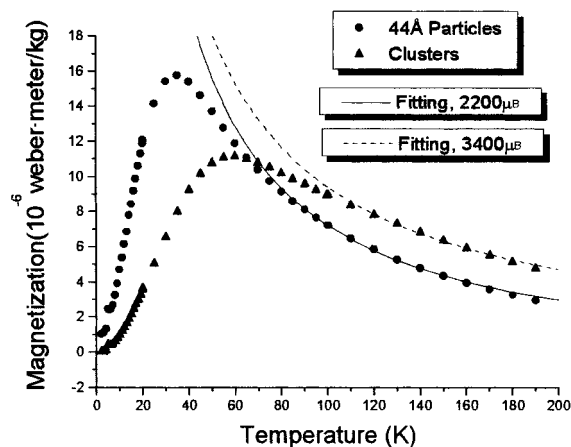


Figure 5. Magnetization versus temperature after zero-field cooling for single particles and clusters. Solid and dashed lines represent the fitting curves of the Langevin function with different μ_{p0} values. The applied magnetic field is 1.59×10^4 A/m.

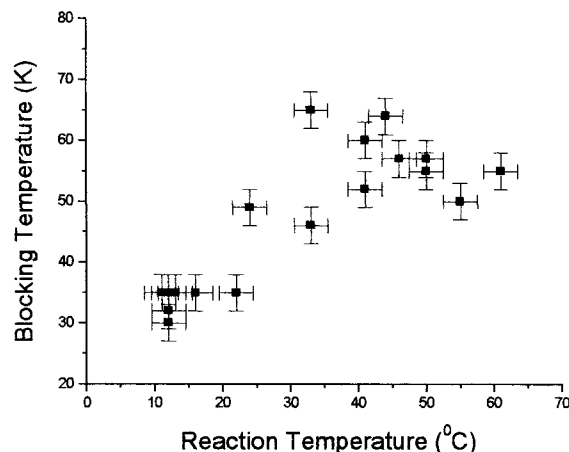
atures are around 32 K, while the T_B values for the clusters are around 55 K. Higher blocking temperatures for the clusters imply that the energy barriers which hinder the moment rotation are larger for the clusters than for the single particles. Below the blocking temperature, ZFC magnetization of clusters is lower than that for the single particles (Figure 5), which also indicates that a smaller fraction of clusters can overcome the higher energy barriers and align with the applied field. The increase of

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Table 1. Properties of Cobalt Nanoparticles and Clusters

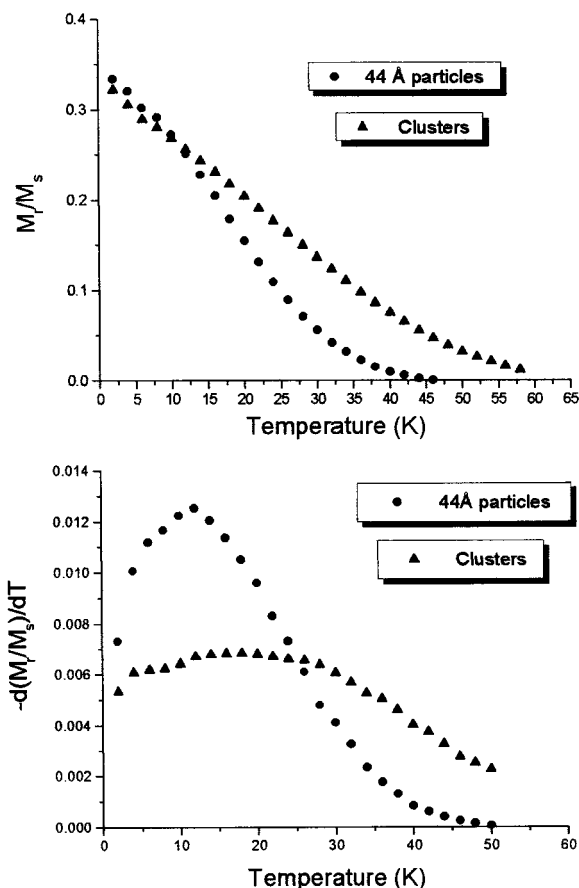
designated samples	T_{rea} (°C)	T_B (K)	μ_{p0} (μ_B)	K (10^5 J/m ³)
Co-057A	12	32	1400	2.8
Co-057B	22	35	2000	0.9
Co-057C	33	46	3400	
Co-057D	44	64	5400	
Co-059A	12	32	1500	2.5
Co-059B	23	49	2500	1.6
Co-059C	41	52	3700	
Co-062A	13	35	2200	2.7
Co-062B	22	35	2200	1.2
Co-062C	33	65	4100	
Co-062D	41	60	3400	
Co-065A	12	30	1600	2.6

^a T_{rea} is the reaction temperature.

**Figure 6.** Blocking temperature for Co single particles and clusters synthesized at different reaction temperatures.

the energy barrier is not a result of the increase of the overall volume of clusters compared with single particles, since the monomer moments inside the cluster are not coupled ferromagnetically, as we pointed out before. Therefore we believe that it is a direct consequence of dipolar interaction inside the cluster. The theoretical calculation done by El-Hilo et al.²⁷ showed that dipolar interaction can increase the energy barrier and therefore increase the blocking temperature of the nanoparticle system. Several experiments^{27,28} based on varying the concentration of the nanoparticles and therefore changing the interparticle interaction also confirmed this theoretical prediction. Our system provides another example that an increase of blocking temperature can occur due to the dipolar interaction. But instead of varying the particle concentration by dilution, clusters are formed directly through chemical synthesis in our experiments.

A direct way of probing the energy barrier distribution is through measuring the decay of the remanence curve with temperature. The sample was first cooled to 2 K in zero field. After saturating the sample using a 4.38×10^6 A/m field, we removed the field and the remanent magnetization was measured. The sample was then warmed, and at each temperature, the remanent magnetization was measured after removing the saturating field. Figure 7a plots the change of the normalized remanence with temperature for both the single particles

**Figure 7.** (a, top) Normalized remanence curve for single particles synthesized at 13 °C and clusters formed at 41 °C. (b, bottom) The derivative of the normalized remanence curve with temperature for both single particles and clusters. M_r is the remanent magnetization, and M_s is the saturation magnetization.

and the clusters and shows that the remanence for the single particles decreases much faster than that for the clusters as the temperature increases. Remanent magnetization arises from the blocked particles whose moments cannot undergo reversal after we remove the saturating field. In general, the normalized remanent magnetization is given by²⁹

$$M_r/M_s = \int_{\Delta E_{\text{crit}}}^{\infty} f(\Delta E) d\Delta E \quad (3)$$

where M_r is the remanent magnetization, M_s is the saturation magnetization, ΔE is the energy barrier, and ΔE_{crit} is the critical energy barrier above which thermal energy can induce switching of the magnetic moment. Since ΔE_{crit} is directly proportional to the measuring temperatures, the derivative of normalized remanent magnetization with temperature will give the distribution of the critical energy barrier.

$$f(E_{\text{crit}}) \sim -\frac{d(M_r/M_s)}{dT} \quad (4)$$

Figure 7b shows the energy barrier distribution for both single particles and clusters. It shows that energy barriers

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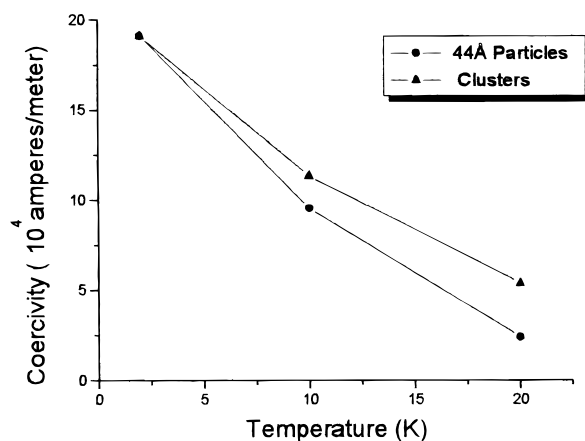


Figure 8. Coercivity as a function of temperature for single particles synthesized at 13 °C and clusters formed at 41 °C.

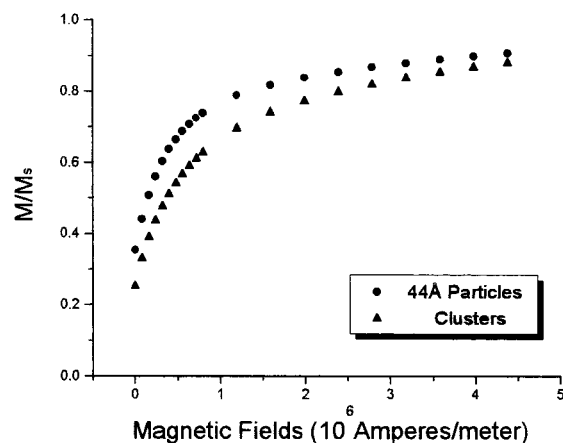


Figure 9. Normalized magnetization versus magnetic field curves at 2 K for Co single particles and clusters. M_s is the saturation magnetization.

for single particles are relatively low in energy and have a narrow distribution, while clusters have a relatively

broader distribution of energy barriers and shift toward higher energy.

The numerical simulation done by Ferre et al.³⁰ showed dipolar interaction would alter the hysteresis curve. More specifically, dipolar interaction increases the coercivity and slows the saturation process by the applied field. Figure 8 shows that the coercivity of the clusters is larger than that of the single particles of which they are made. Figure 9 displays magnetization versus field curves for single particles and clusters and shows that clusters are more reluctant to reach saturation. All these data prove that dipolar interactions are present among monomers in the cluster sample prepared at high reaction temperature. The interaction effect has to be taken into account in order to interpret the magnetic properties of the cluster system.

4. Conclusion

Cobalt nanoparticles have been synthesized in DDAB/water/toluene inverse micelle solution with [water]/[DDAB] = 5:1. Low reaction temperatures yielded isolated spherical particles, while high reaction temperatures yielded clusters with a limited number of monomers. Single cobalt particles have an enhanced magnetic anisotropy constant compared with that for the bulk cobalt. Clusters have a higher blocking temperature and a reduced effective moment compared with those of their single-particle components due to the dipole–dipole interaction between the single-particle components.

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