Temperature dependence of magnetic properties of SiO$_2$-coated Co nanoparticles

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Abstract

SiO$_2$-coated Co nanoparticles were synthesized; the different temperature-dependent magnetic behaviors between Co nanoparticles with and without inner Co-oxide cores were observed. For Co nanoparticles free of Co-oxide cores, the magnetization obeyed Bloch’s $T^{3/2}$ law with a Bloch constant close to the bulk value; the coercivity exhibited a weak and linear dependence on temperature. For Co nanoparticles with Co-oxide cores, the Bloch exponents fell from 1.5 to smaller values and decreased with increasing Co-oxide concentration; the coercivity significantly increased with decreasing temperature due to the presence of exchange anisotropy, which arose from the exchange coupling across the Co/CoO interfaces.

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1. Introduction

Understanding the temperature dependence of magnetic properties in ferromagnetic nanoparticles is an important issue in magnetic materials. The temperature-dependent magnetic properties of Fe nanoparticles have been extensively studied; the different temperature behaviors between oxide-coated Fe nanoparticles and pure Fe nanoparticles (free of surface oxidation) have been experimentally observed [1–4]. Xiao et al. studied the magnetization temperature dependence of Fe nanoparticles embedded in SiO$_2$ and found that the pure Fe nanoparticles followed Bloch’s law with a Bloch exponent of bulk Fe ($b = 1.5$) and a Bloch constant $B$ substantially larger than that of bulk Fe [2]. Banerjee et al. looked the oxide-coated Fe nanoparticles and found that their Bloch exponent was significantly smaller than 1.5 due to the presence of oxide shell [3]. Gangopadhyay et al. studied the influence of surface oxidation on the coercivity temperature dependence of Fe nanoparticles and found that the coercivity for the Fe nanoparticles with high oxide concentration was high at low temperature and decreased drastically with increasing temperature, while that for the Fe
nanoparticles with low oxide concentration exhibited a weak dependence on temperature [4]. The temperature dependence of oxide-coated Co nanoparticles has also been investigated. The drastic decrease in magnetization with increasing temperature was observed, and the value of coercivity was found to increase significantly with decreasing temperature and starts to decrease at a temperature of about 80 K [5]. However, the temperature-dependent properties of Co nanoparticles without surface oxidation have never been reported. In this paper, we present the temperature dependence of magnetic properties of two kinds of nanoparticles: (1) pure Co nanoparticles and (2) Co nanoparticles with inner Co-oxide core. Both of them are protected from surface oxidation by an SiO$_2$ coating.

2. Experimental

Co nanoparticles were synthesized by a wet chemical technique. The detailed synthesis procedure was presented elsewhere [6,7]. The key step in the procedure was to convert SiO$_2$-coated Co$_3$O$_4$ nanoparticles to SiO$_2$-coated Co nanoparticles through a low-temperature calcination. Our previous works [8] indicated that when the calcination temperature was as high as 900°C, the synthesized nanoparticles had a core/shell structure: the core was FCC Co and the shell was amorphous SiO$_2$. When the calcination temperature was 800°C or below, the synthesized nanoparticles had a nano-onion structure: the first shell was amorphous SiO$_2$, the second shell was FCC Co, and the inner core was Co$_3$O$_4$ with a thin CoO coating.

Co particle sizes were estimated from the X-ray diffraction peak using Scherrer formula. Magnetic properties were studied using a Quantum Design SQUID magnetometer. Saturation magnetization was determined by $H^{-1} \rightarrow 0$ extrapolation using fields of $H \leq 55$ K Oe.

3. Results and discussion

Four nanoparticle specimens were synthesized by using the same precursors but different calcination temperatures. Their particle sizes and saturation magnetizations at 5 K are given in Table 1. Specimen A0 did not contain Co-oxide cores and its saturation magnetization reached the expected value for Co$_{50}$/(SiO$_2$)$_{50}$ (volume fraction). Specimens A1, A2, and A3 had Co-oxide cores. From their calcination temperatures and saturation magnetizations, we anticipated that specimen A1 had the smallest oxide core and specimen A3 had the biggest oxide core.

The variations of saturation magnetization as a function of temperature for four specimens are shown in Fig. 1 and are found to obey Bloch’s law [1,9]

\[
M(T) = M(0)(1 - BT^b) \quad (for \ T \ll T_c),
\]

where $B$ is Bloch constant and $b$ is Bloch exponent. The values of $B$ and $b$ for four specimens were obtained by fitting the measured data to Eq. (1) and were given in Table 2. The values of $B$ and $b$ for bulk Co were reported to be $3.3 \times 10^{-6} K^{-3/2}$ and 1.5, respectively [9]. As shown in Table 2, the Bloch exponent of specimen A0 approached that of bulk Co. That is to say, Co nanoparticles without oxidation fitted Bloch’s $T^{3/2}$ law as bulk Co did. This result is not very surprising, because we are concerned with temperatures much lower than the Curie temperature of Co (1404 K) and the spin-wave theory holds quite well in this temperature regime. This result is also consistent with that for Fe nanoparticle. Xiao et al. found $b = 1.5$ for Fe nanoparticles protected by SiO$_2$ [2]. From Table 2 it also can be seen that specimen A0 exhibited a small Bloch constant of $3.49 \times 10^{-6} K^{-3/2}$, which is very close to the Bloch constant for bulk Co and implies a weaker dependence of magnetization on temperature.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Calcination temperature (°C)</th>
<th>Particle size (nm)</th>
<th>Saturation magnetization at 5 K (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>900</td>
<td>39.8</td>
<td>132.7</td>
</tr>
<tr>
<td>A1</td>
<td>800</td>
<td>24.6</td>
<td>122.0</td>
</tr>
<tr>
<td>A2</td>
<td>700</td>
<td>22.8</td>
<td>84.8</td>
</tr>
<tr>
<td>A3</td>
<td>600</td>
<td>22.1</td>
<td>69.9</td>
</tr>
</tbody>
</table>
Differing from specimen A0, however, specimens A1, A2, and A3 failed to fit Bloch’s $T^{3/2}$ law. Their Bloch exponents were significantly smaller than that for bulk Co and decreased with increasing Co-oxide concentration, while their Bloch constants were notably bigger than that for bulk Co and increased with increasing Co-oxide concentration. These results are in good agreement with those reported previously in Ref. [3], where Banerjee et al. found that the values of the Bloch exponents for Fe nanoparticles were less than 1.5 and decreased with increasing surface iron oxide concentration. These results imply that there is a stronger dependence of magnetization on temperature and are believed to be due to the presence of $\text{Co}_3\text{O}_4$ and CoO and their magnetic transition from anti-ferromagnetic and/or super-paramagnetic to paramagnetic with increasing temperature. It should be noted that the Bloch parameters for specimen A3 were based on the data analysis over 50–350 K; in the 5–50 K temperature range, the magnetization of specimen A3 exhibited a more pronounced temperature dependence due to high $\text{Co}_3\text{O}_4$ concentration.

Fig. 2 shows the coercivity versus temperature for four specimens. It is evident that the coercivity for specimen A0 was linearly and weakly dependent on temperature with a slope of $-0.191 \text{ Oe/K}$, though its value was relatively higher than that of bulk Co. Bonder et al. reported that the coercivity for Ni nanoparticles protected from oxidation by $\text{Ni}_3\text{C}$ also exhibited a linear temperature dependence but with a relatively steep slope of $-1.35 \text{ Oe/K}$ [10].

Different from specimen A0, specimens A1, A2, and A3 exhibited a stronger dependence of coercivity on temperature. With decreasing temperature, the coercivity increased significantly, especially in the 50–250 K temperature range. There are two reasons for this behavior. One is that since the effective Co particle sizes of specimens A1, A2, and A3 were relatively small (compared with specimen A0) due to the presence of oxide cores, some small particles underwent a magnetic transition from superparamagnetic to ferromagnetic with decreasing temperature. Another reason is the presence of the exchange anisotropy, which arises due to the exchange coupling across the Co/CoO interfaces.

It is known that bulk CoO is anti-ferromagnetic with a Neel temperature of $T_N = 270 \text{ K}$ [11]. But in our nanoparticles most of CoO layers were believed to be so thin that they exhibited super-paramagnetism at 270 K or below. Thicker CoO layers underwent a superparamagnetic to anti-ferromagnetic transition at a temperature (blocking temperature) near 270 K, while thinner CoO layers did that at a temperature well below 270 K. As a result, the increase of the exchange anisotropy (with decreasing temperature) occurred over a wide temperature range (below 270 K). Fig. 3
shows the exchange field (the shift of field-cooled loop) [11] versus temperature for specimen A3, which was measured after a field cooling from 350 K to measurement temperature under 55 K Oe. It reveals that the exchange field started to appear around 250 K and increased with decreasing temperature over a wide temperature range from 250 to 20 K. This result confirms the above postulate that the superparamagnetic to antiferromagnetic transition of CoO happened over a wide temperature range. The significant increase in coercivity over 50–200 K for specimens A1, A2, and A3 is believed to arise mainly due to the increase of exchange anisotropy. The more pronounced dependence of coercivity on temperature for specimen A3 can be ascribed to the larger Co/CoO interfaces.

It also can be seen from Fig. 2 that, with decreasing temperature, the coercivity for specimen A3 increased and then started to decrease below 50 K. Similar temperature behavior has also been observed in oxide-coated Co nanoparticles [5]. The reason for this behavior may be attributed to high CoO concentration in the nanoparticles. Bulk CoO exhibits an antiferromagnetic behavior below its Néel temperature of \( T_N = 33 \) K, [12] while the CoO cores in our nanoparticles might exhibit a superparamagnetic behavior below 33 K due to small size, which might weaken the exchange coupling between Co and CoO.

In addition, it can be known from Fig. 2 that the coercivity decreases with increasing effective Co particle size even in the temperature range of 250–350 K where the exchange anisotropy no longer existed. This result is consistent with the theoretical analysis given in Ref. [11], where O’Handley argued that the coercivity went as \( H_C \approx a/r^2 - b \) (\( r \), particle size) for non-interacting single-domain particles. The Co nanoparticles in our specimens were free of interaction and their sizes were smaller than the single-domain critical size (76 nm) of FCC Co [13].

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References