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Magnetic properties in $CeCo_2$ nanoparticles

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Abstract

Bulk $CeCo_2$ is characterized as a Pauli paramagnet, both Ce and Co are essentially nonmagnetic. The data of $\chi(T)$ show that $CeCo_2$ nanoparticles exhibit extremely complex magnetic properties. Two magnetic phases, a major paramagnetic component and a minor ferromagnetic component, were detected in $CeCo_2$ nanoparticles. A superparamagnetic behavior was shown at $T > 200$ K and a low-temperature spin-glass-like behavior was observed at $T = 10-30$ K. Such magnetic changes were attributed to the size effects in nanoparticles.

Keywords: Superparamagnetism; Paramagnetism; Spin glass; Nanoparticle

1. Introduction

$CeCo_2$ is a superconducting compound with $T_c = 0.9-1.5$ K. The extremely low value of its magnetic susceptibility indicates that, in this compound, both Ce and Co are essentially nonmagnetic and Ce is very likely in an intermediate valence state [1,2]. XPS and Ce L_{III} X-ray absorption edges further specify that the electronic configuration of Ce in the bulk is nonmagnetic Ce^{4+}, whereas the surface ions of Ce can be both Ce^{3+} and Ce^{4+} [3]. Since the unusual nonmagnetic behavior of $CeCo_2$ is significantly dissimilar from the usually observed ferromagnetic or antiferromagnetic Ce- and Co- based compounds, this reflects that the electronic configuration of nonmagnetic superconducting $CeCo_2$ might be at a novel metastable state. If the metastable state is perturbed by certain factors such as external pressure, or particle size reduction, it might be driven back to a normal stable magnetic state as commonly seen in (Ce,Co) compounds. In order to accomplish this goal, we prepared $CeCo_2$ nanoparticles and performed the measurements of magnetic susceptibility $\chi(T)$ and magnetization $M(H)$ at various temperatures to investigate how the nonmagnetic properties of $CeCo_2$ were influenced by the size effects.

2. Experiments and analysis

$CeCo_2$ nanoparticles were fabricated by flash evaporation of $CeCo_2$ bulk in a 0.1 Torr helium atmosphere, the details of sample preparation were described in an early report for $CeAl_2$ nanoparticles [4]. According to the X-ray diffraction patterns (Fig. 1), there was no difference in structure between particles and parent bulk material, except a slight trace of CeO_2 in nanoparticles, but at a level not exceeding 10%. Nevertheless, the characteristic reactivity of fine particles, along with the high oxidation susceptibility of Ce, could likely lead to a thin layer of CeO_2 on the surface.

Based on transmission electron microscopy (TEM) images, an average diameter for $CeCo_2$ nanoparticles was estimated to be 100 Å. An example of the high-resolution transmission electron microscopy (HRTEM) images (inset of Fig. 1) reveals several well-crystallized spherical particles and shows the clear lattice arrays of $CeCo_2$. The measurements of magnetic susceptibility $\chi(T)$ and magnetization $M(H)$ were implanted in a superconducting quantum interference device (SQUID).

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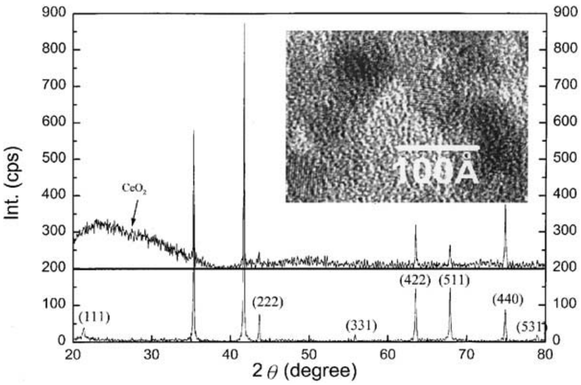

Fig. 1. The X-ray diffraction patterns of $CeCo_2$ nanoparticles (the top) and $CeCo_2$ bulk (the bottom). The bump at $2\theta \sim 20$–35° is the background of grease for sample attachment. A blurred anomaly around $2\theta = 28.6^\circ$ on top of the background corresponds to the main (1 1 1) peak of CeO_2; inset: the HRTEM image of $CeCo_2$ nanoparticles.

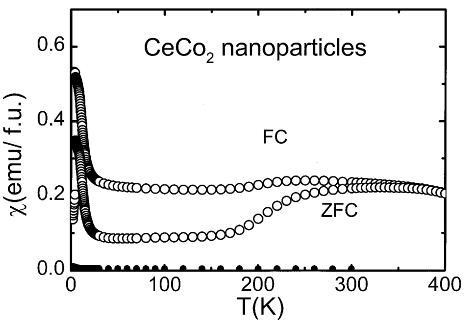

Fig. 2. ZFC and FC magnetic susceptibility of $CeCo_2$ nanoparticles under $H = 200\,G$ (open circles) and the magnetic susceptibility of $CeCo_2$ bulk under $H = 1000\,G$ (solid circles).

The magnetic susceptibility of $CeCo_2$ nanoparticles exhibits extremely complex magnetic features as compared with the bulk $CeCo_2$ (Fig. 2). At high temperatures, a wide bump peaked at 300 K is noticed. After a flat region at intermediate temperatures, a low-temperature anomaly emerges with a maximum at about 5–7 K. The high-temperature anomalies of ZFC and FC magnetic susceptibility, are identified as superparamagnetism; a similar phenomenon is commonly seen in fine magnetic powders [5]. The blocking temperature T_b of the superparamagnetism is estimated to be about 350 K. The magnetization data for various temperatures give the evidence that the two phases, i.e., ferromagnetism and paramagnetism coexist (Fig. 3). If the ferromagnetic phase is a Co element or a Co relevant alloy with a saturated magnetization ~ 20000 emu/f.u., then, the concentration of the ferromagnetic phase corresponding to the saturated magnetization is estimated to be about 0.5 at%, according to the saturated magnetization

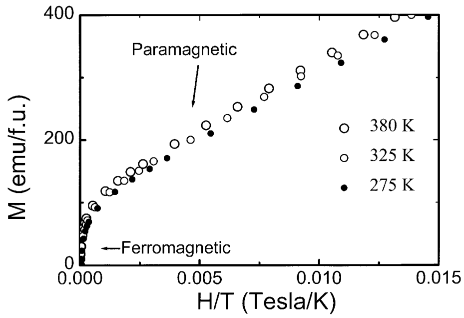

Fig. 3. The magnetization of $CeCo_2$ nanoparticles versus H/T for several temperatures.

~ 100 emu/f.u. at $H_s = H/T \sim 5 \times 10^{-4}$, H_s is the field where magnetization saturates (indicated by the arrow in Fig. 3).

In the display of magnetic susceptibility, due to the superposition of the ferromagnetic phase and the paramagnetic phase, estimating the effective magnetic moments of the paramagnetic phase through simple Curie–Weiss law becomes unfeasible. The temperature-dependent magnetic susceptibility of paramagnetic phase is then reconstructed indirectly by the field derivative of $M(H, T_0)$ for each temperature, i.e., $\chi(T_0) = \partial M/\partial H$ for $H > H_s$. In Fig. 4, the extracted χ's thus obtained for each particular temperature are plotted and fitted to a Curie–Weiss relation $C/(T-\theta)$ with $C = 2.29$ emu K and $\theta = -48$ K. The reduced effective magnetic moment μ_{eff} derived from the Curie constant C is $2.98\,\mu_B$/f.u. In comparison with the individual magnetic moment $2.54\,\mu_B$/f.u. of Ce^{3+} and $\sim 1\mu_B$/f.u. of Co element, we conclude that in $CeCo_2$ nanoparticles, both Ce and Co are essentially magnetic, this consequence is in contrast to the bulk $CeCo_2$.

As shown by the data of magnetic susceptibility in Fig. 2, the paramagnetic phase persists to very low temperatures before reaching the region where the low-temperature anomaly prevails. The reduced effective magnetic moment μ_{eff} at $T = 30$ K is estimated from the fit of low-temperature magnetic susceptibility (20–50 K) to the Curie–Weiss relation $C/(T-\theta)$ to be $\sim 1.57\,\mu_B$/f.u. The reduction in effective magnetic moment can be explained by the crystal field splitting as commonly seen in magnetic (Ce,Co) compounds [6].

In the measurements of ZFC and FC magnetic susceptibility at $T < 20$ K, the separation of magnetic susceptibility appears at 7 and 12 K for $H = 50$ and 500 G, respectively. The phenomena reveal that the low-temperature anomaly is likely a spin-glass behavior with a frozen temperature $T_f \sim 10$ K. The magnetic moments of the spin-glass-like behavior is conjectured to be associated with those of the paramagnetic phase mentioned early at higher temperatures.

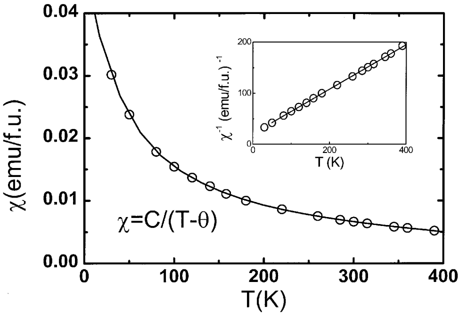

Fig. 4. The extracted χ's fitted to a Curie–Weiss law represents a paramagnetic phase in $CeCo_2$ nanoparticles.

3. Conclusion

In this work, we observe that $CeCo_2$ undergoes a nonmagnetic and a magnetic phase transition induced by the size reduction. The low-level (≈ 0.5 at%) unidentified ferromagnetic phase could be elemental Co or (Ce,Co) compound formed during the fabrication of nanoparticles. The ferromagnetic component in nanoparticles gives rise to a super-paramagnetic behavior at $T > 200$ K with $T_b \approx 350$ K. The existence of a paramagnetic phase having a reduced effective magnetic moment $\mu_{eff} = 2.98\,\mu_B$/f.u. indicates that both of Ce and Co in $CeCo_2$ nanoparticles possess magnetic moments. Owing to the crystal-field splitting, the effective magnetic moment μ_{eff} is reduced to $1.57\,\mu_B$/f.u. at $T \approx 35$ K. As temperature decreases to about 20 K, a phase transition of paramagnetism to spin-glass behavior is observed. It is concluded that the size and surface effects play important roles in the complicated magnetic behaviors in $CeCo_2$ nanoparticles.

Acknowledgements

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