Antiferromagnetic $CoRh_2O_4$ Nanoparticle: A Unique System to Study Surface Magnetism

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We report the enhancement of magnetization below the antiferromagnetic ordering temperature T_N in $CoRh_2O_4$ nanoparticles. Scaling analysis shows that such an enhancement of magnetization in antiferromagnetic nanoparticles is due to the superparamagnetic type contribution of surface spins. Recently, we have seen an unusual behaviour that $CoRh_2O_4$ nanoparticles exhibited in zero field cooled magnetic relaxation at low temperature, which will be briefly discussed here.

1. Introduction

Research interest for magnetic nanoparticles are growing up due to their potential applications in nanoscience and technology, as well as theoretically to understand the structural and magnetic modifications taking place for particle dimension of atomic scale [1,2]. According to core-shell model of ferrimagnetic nanoparticle, proposed by Kodama et al. [4], the decrease of particle size leads to the decrease of magnetic order and magnetization due to the increasing surface disorder in nanoparticles. The surface disorder has shown many interesting phenomena like superparamagnetism, and exchange bias effect [2]. On the other hand, antiferromagnetic nanoparticles exhibited increase of magnetization below their Néel temperature (T_N), unlike the decrease in bulk, with further decrease of temperature. Such an increase in magnetization in antiferromagnetic particles is unusual in comparison with the ferromagnetic nanoparticles. Such behaviour has been attributed to either induced ferromagnetism or superparamagnetism, resulting in from increasing uncompensated surface spins in nanoparticles [3]. We show similar enhancement of magnetization below T_N in nanoparticles of $CoRh_2O_4$, which belongs to cubic spinel structure.

2. Experimental

We obtained nanoparticles by mechanical milling of the bulk material $CoRh_2O_4$ using Fritsch Planetary Mono Mill "Pulverisette 6". Bulk $CoRh_2O_4$ was obtained by conventional high temperature (at 1000^0C for 12 hours and at 1200^0C for 48 hours) sintering method. A typical spinel structure of the bulk and nanoparticle $CoRh_2O_4$ were confirmed by XRD spectra. We have seen the decreases of particle size of the sample with increase of milling hours. This was confirmed from TEM data. After 60 hours milling, we obtained particle size ~16 nm. DC magnetization data were measured using SQUID (Quantum Design, USA) magnetometer.

3. Results and discussion

Fig. 1 shows the zero field cooled magnetization data for bulk and nanoparticle $CoRh_2O_4$ samples, measured at 100 Oe. The antiferromagnetic ordering at $T_N \approx 27$ K of bulk is also retained for nanoparticle samples. The notable feature is that all of the nanoparticle samples show the enhancement of magnetization below T_N. This feature is not consistent with the usual core-shell model [4], which stated the decrease of magnetization with the decrease of particle size.

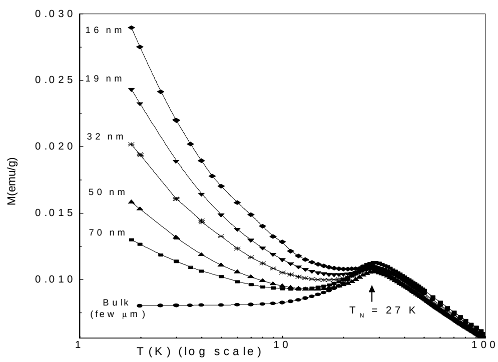

Fig. 1 Temperature dependence of ZFC magnetization at 100 Oe (semi-log plot) for bulk and nanoparticles of $CoRh_2O_4$. T_N is antiferromagnetic ordering temperature

Similar low temperature increase of magnetization T_N may be due to the ferrimagnetic or superparamagnetic type contributions in antiferromagnetic nanoparticles [3]. The log-log plot of H/M vs T data (Fig. 2a) shows that H/M ∝ T^γ below 10 K for nanoparticles with γ systematically increases from 0.23 (for 70 nm) to 0.49 (for 16 nm). The exponent γ is, still, far below 1 for a typical paramagnet/superparamagnet. We attribute this deviation to the coexistence of frustrated shell spins and antiferromagnetic core spins [5]. The increase of γ with the decrease of particle size indicates that the shell contribution is increasing with the decrease of particle size.

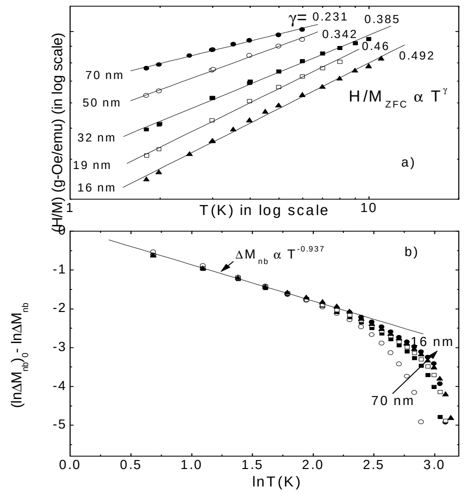

Fig.2 a) H/M vs T^{γ} below 10K for nanoparticle samples.
b) magnetization of nanoparticles over bulk sample (ΔM_{nb}) follows a scaling law upto 10K and deviates at higher temperature.

We minimized the contribution of antiferromagnetic core by subtracting the MZFC of bulk sample from the MZFC of each nanoparticle samples, assuming core magnetic contribution is identical to the bulk, which is quantifies as $\Delta M_{nb} = (MZFC)_{nano} - (MZFC)_{bulk}$. We, then, determine the value of ΔM_{nb} at limit T = 0 K , (i.e. $(\Delta M_{nb})_0$) from the linear extrapolation of ln (ΔM_{nb}) vs ln (T) plot. We see (Fig. 2b) that MZFC below 10 K obeys the scaling law: $\Delta M_{nb} = \Delta M_{nb})_0 T^{-0..94}$. The exponent is still below 1, and indicates that the antiferromagnetic order of core is still affecting the superparamagnetic behaviour of the shell. We have also found similar enhancement of magnetization for Cr_2O_3 nanoparticles below the antiferromagnetic ordering temperature 300 K for bulk sample [6].

We now show some of the interesting magnetic behaviour that our $CoRh_2O_4$ nanoparticles exhibited in ZFC magnetic relaxation at low temperature. Each sample was zero field cooled from 70 K to the measurement temperature at 2 K. After temperature stabilization, 100 seconds waiting time was given to the sample before application of 100 Oe and start of the recording of magnetization as a function of time. The M(t) data are shown in Fig. 3. Fig. 3 shows that ZFC magnetization at 2 K decreases with time, even though the magnetic field is ON. This happens down to a typical particle size ~ 19 nm. However, 16 nm sample shows as usual increase of ZFC magnetization with time in the presence of magnetic field.

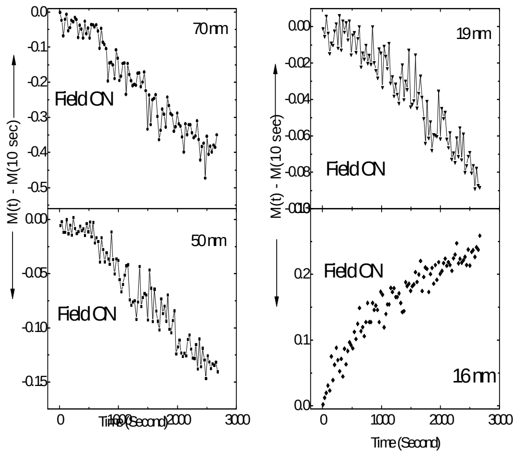

Fig. 3 Time dependence of magnetization for CoRh2O4 nanoparticle in presence of 100 Oe Field during measurement

Such time relaxation of ZFC magnetization is really interesting and possibly seen for the first time in any magnetic system. A few more unique features of the relaxation behaviour will be discussed elsewhere

4. Conclusions

It is concluded that the total magnetization of the antiferromagnetic nanoparticle $M = M_{core} + M_{shell}$, where M_{core} is magnetic contribution from core spins and M_{shell} is magnetic contribution from shell spins. The shell (surface) contribution increases with the decrease of particle size. The analysis of the magnetization data suggests that the enhancement of magnetization below T_N of antiferromagnetic nanoparticles arises from the magnetic contributions of surface spins. We believe that the unusual ZFC magnetic relaxation in larger antiferromagnetic ($CoRh_2O_4$) nanoparticles arosed due to some competitive effects in surface spins. Details will be reported elsewhere.

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