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The study of entropy change and magnetocaloric response in magnetic nanoparticles via heat capacity measurements

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ABSTRACT

In our work, we have investigated the magnetocaloric effect (MCE) of core@shell Co@Au nanoparticles by heat capacity C_p measurement in temperature range 1.9–55 K under external magnetic field. After the subtraction of lattice heat capacity contribution, the maximum of isothermal magnetic entropy change $\Delta S_m = 3.11$ J K^{-1} kg^{-1} was obtained at field change from 0 to 9 T. Adiabatic temperature change $\Delta T_{ad} = 3.31$ K, refrigerant capacity power RCP = 88.9 J kg^{-1} and efficiency of adiabatic temperature change $\eta = 0.37$ K/T at the same external magnetic field change were established for the investigated system. The comparison of the results to the independent magnetic measurements data revealed the accordance of fundamental magnetocaloric characteristics obtained by both methods. Thus, this work is also the first experimental confirmation of relation between magnetocaloric response of nanoparticles and the low temperature magnetic transition from superparamagnetic to blocking/freezing state.

1. Introduction

Wide variety of magnetic materials are currently being applied as essential parts in number of devices (permanent magnets, electromotors, memory media, transducers) as well as in environmental and industrial technologies saving both resources and energy (Aprea et al., 2015; Aprea et al., 2017; Giri et al., 2005; Jiles, 2003; Sun et al., 2000; Teyber et al., 2017a). Magnetic refrigeration can be regarded as one of the most expanding scope of magnetic research in last years (Franco et al., 2012). Utilization of magnetic material as refrigerant stems in the effect discovered by Weiss and Piccard in 1917 (Weiss and Piccard, 1917). The behavior denoted as magnetocaloric effect (MCE) is currently being understood as isothermal entropy change or adiabatic temperature change of magnetic solids induced by the variation in external magnetic field applied on such material (Gschneider et al., 2005; Teyber et al., 2017b). An effort to design suitable magnetic refrigerator is driven by the demand of finding the alternative cooling technology applicable from room temperature to the cryogenic temperature regime (Gschneider, 2002). In particular, magnetic refrigeration with its energy-efficient and environment-friendly advantages offers the perspective to replace the present vapor-cycle refrigeration technology dominance. Nowadays, magnetic refrigeration has become one of the basic technologies for getting ultra-low temperatures (Shen et al., 2009). Despite of high attention focused on magnetocaloric materials design, there is relatively a little work devoted to the exploration of the properties of nanoparticle clusters or assemblies with respect to MCE. It is known that nanoparticles exhibit fundamentally different properties in comparison with their bulk or thin film counterparts (Reddy et al., 2012). In general, the origin of such distinct behavior is the consequence of size effects. For instance, in the case of nanoparticles from ferromagnetic material, after reducing the size of the particle below the critical value, the particle favors to preserve the single domain state. Thus the particle exhibits large magnetic moment (superspin) what reflects in peculiar properties of systems consisting of these particles. High saturation magnetization, typical of ferromagnets, contrary to the absence of magnetic hysteresis, remanence or coercivity is the characteristic of such systems (Provenzano et al., 2004). Surprisingly, despite of profound research on core@shell magnetic nanoparticles in the area of biomedicine (Chatterjee et al., 2014), the comprehensive magnetocaloric properties studies of this kind of systems are almost absent. Despite of the lack of reports devoted to magnetocaloric properties of nanoparticles, the trends of employing systems of this kind in perspective fields like hyperthermia treatment or nano-refrigeration are significant (Nair et al., 2016; Tishin and Spichkin, 2014; Tishin et al., 2016). Understanding of the correlation between fundamental magnetization

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Nomenclature

C_P	heat capacity at constant pressure (J K^{-1} kg^{-1})
$C_{p,\,H}$	heat capacity at constant pressure and external magnetic field (J K^{-1} kg^{-1})
d_{TEM}	average diameter obtained by transmission electron microscopy (m)
FC	field vooling
FWHM	full width at half maximum
H	external magnetic field (T)
lat	lattice
M	magnetization (A m^2)
mag	magnetic
MCE	magnetocaloric effect
PPMS	physical properties measurement system
RCP	refrigerant capacity power
T	temperature (K)
T_B	blocking temperature
TEM	transmission electron microscopy
tot	total
ZFC	zero field cooling
ΔS_m	magnetic entropy change (J K^{-1} kg^{-1})
ΔT_{ad}	adiabatic temperature change (K)
η	efficiency of adiabatic temperature change (K/T)
μ_0	vacuum permeability
Subscripts and superscripts	
H_0	constant external magnetic field
H_1	constant external magnetic field
MAX	maximum
ΔH	external magnetic field change

processes and magneto-thermal responses can help to improve and tune the applicability of magnetic nanoparticles.

The evaluation of magnetocaloric effect in nanoparticle systems is usually being carried out by means of magnetic entropy change ΔS_m calculations derived from isothermal M(H) data (Reddy et al., 2012; Provenzano et al., 2004; Chatterjee et al., 2014; Hrubovčák et al., 2017; Poddar et al., 2007). However, in the case of specific magnetic systems with the presence of thermal hysteresis, the application of Maxwell thermodynamic relations may introduce non-physical artifacts in temperature dependence of ΔS_m. This problem can be avoided by means of MCE evaluation via direct measurements of heat capacity.

Since there is a lack of studies devoted to the investigation of magnetocaloric properties of nanoparticle systems employing heat capacity measurements, we decided to examine Co@Au core@shell nanoparticles from this point of view. Magnetocaloric properties of Co@Au system have been studied by heat capacity measurement $C_P(T)$ in temperature range 1.9–55 K. We have examined the system in terms of isothermal magnetic entropy change ΔS_m, adiabatic temperature change ΔT_{ad}, refrigerant capacity power RCP and efficiency of adiabatic temperature change at external magnetic field change η. In addition, the results of present study suggest the relation between the MCE enhancement and superparamagnetic to superspin glass state transition documented in Co@Au nanoparticle system (Hrubovčák et al., 2015). The abrupt change of magnetic entropy induced by the change from equilibrium to non-equilibrium dynamics of particles' superspins at transition temperature is assumed to be the origin of this phenomenon.

2. Experimental

Core@shell Co@Au nanoparticles were prepared using microemulsion method in reverse micelles (Lin et al., 2001). Individual nanoparticles with nearly spherical shape and average diameter $d_{TEM} \sim 7$ nm were observed by TEM (Hrubovčák et al., 2015). The temperature and magnetic field dependence of the heat capacity at constant pressure C_p were measured using the heat capacity option in PPMS by Quantum Design in temperature range 1.8–55 K and applied magnetic fields from 0 to 9 T. The powder sample (8 mg) was pressed to form a pellet and then a very small amount of grease (Appiezon N) was used to make proper thermal contact between the pellet and a sample platform. The magnetocaloric response of the system represented by isothermal entropy change ΔS_m and adiabatic temperature change ΔT_{ad} was calculated from heat-capacity data after subtracting addenda signal and the lattice contribution to total heat capacity.

3. Results and discussion

The behavior of temperature heat capacity $C_P(T)$ dependence is characterized by a wide peak at 9 K in a zero external magnetic field (Fig. 1). The maximum becomes broader, it shifts to higher temperatures and smears gradually with external magnetic field increase, while it finally disappears in the applied field of 6 T. This kind of behavior indicates that studied Co@Au nanoparticle system may undergo phase transition between two distinct magnetic states (Bishwas and Poddar, 2016). Virtually, the peak position of heat capacity data at temperature $C_P(T) \sim 9$ K occurs at the vicinity of blocking temperature from the range 7–9 K. Blocking temperature is understood as a transition temperature from superparamagnetic to blocking/freezing state of the nanoparticle system and it was established by means of ZFC/FC protocols in our previous study (Hrubovčák et al., 2015). However, the value of blocking/freezing temperature is not absolute from its definition and it depends on the timescale, during which the magnetization was recorded. Moreover, T_B is the function of magnetic field applied on the system. Usually, it is determined experimentally from ZFC measurements and it is assumed as the ZFC M (T) peak position or the temperature, at which ZFC and FC magnetization starts to bifurcate. We assume the mutual closure of blocking/freezing temperature T_B to $C_p(T)$ peak temperature is not accidental and it points to the fact, that the origin of both hallmarks observed (maxima in ZFC and C_p) stems in single phenomenon—magnetic transition from superparamagnetic to superspin glass state. As was mentioned in our previous work (Zelenakova et al., 2014), there is the critical limit for size of nanoparticle from ferromagnetic material, below which it is energetically more efficient for the particle to preserve single domain state. The particle in monodomain state is characterized by huge magnetic moment, superspin. At low temperatures, due

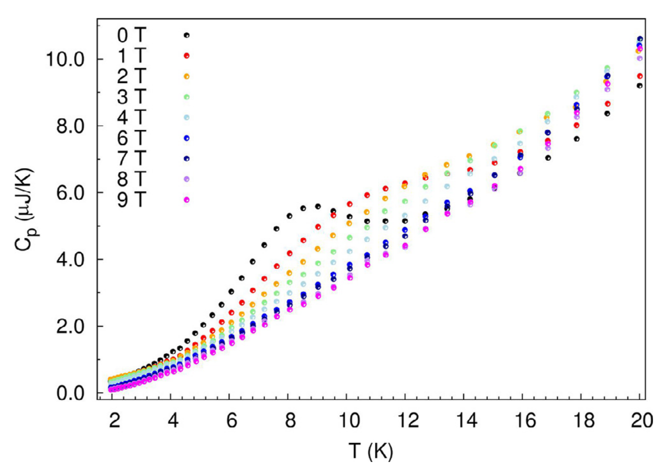

Fig. 1. The heat capacity of Co@Au nanoparticles measured during heating in constant magnetic fields of 0, 1, 2, 3, 4, 6, 7, 8 and 9 T.