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Field dependence of the magnetocaloric effect in core-shell nanoparticles

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The field dependence of the magnetic entropy change peak at the low temperature surface spin freezing transition in chemically synthesized, monodispersed Co, Co–Ag, and Ni–Ag core-shell nanoparticles is studied, with the aim of gaining insight into the critical exponents of this transition. It is evidenced that although the magnitude of the peak entropy change and position of the peak can be tuned by changing the composition and nature (metallic or organic) of the shell and surfactant layers, the characteristics of the spin freezing transition are not altered. The field dependence of the refrigerant capacity also confirms this finding. © 2010 American Institute of Physics. [doi:10.1063/1.3335514]

Magnetocaloric effect (MCE) and its most straightforward application, magnetic refrigeration, are becoming fields of increasing research interest (for recent reviews, the reader can consult Refs. 1–5). The reason for this is twofold. On the one hand, magnetic refrigerators are expected to be energetically more efficient and more environmentally friendly than those based on the compression-expansion of gases, which are extremely important considerations in applied scientific research in an era of increasing energy costs and environmental awareness. On the other hand, as magnetic refrigeration close to room temperature is only possible with materials which undergo a phase transition close to the working temperature of the refrigerator, the characterization of magnetocaloric materials generally tends to become associated with a detailed study of their phase transition, which is also interesting from a fundamental point of view.

Apart from maximizing the magnetocaloric response of specific materials for a certain value of the applied magnetic field, the response of the materials should be optimized for the applied field range (10–20 kOe) which is expected for future refrigerator appliances. Therefore, the study of the field dependence of magnetic entropy change, ΔS_M , is an important subject of research. Recently, the limitation of a mean field approach has been overcome by using the equation of state for materials with a second order magnetic phase transition.^{6,7} Expressing the field dependence as $\Delta S_M \propto H^n$, this approach allows for establishing a relationship between the exponent n and the critical exponents of the material and to propose a phenomenological universal curve for the field dependence of ΔS_M , which was successfully tested for series of soft magnetic amorphous alloys^{6,8} and lanthanide based crystalline materials.^{9,10}

As in many other fields of research, most magnetocaloric materials investigated have primarily been bulk in nature.

However, the emerging interest in novel magnetic behavior of nanostructured magnets can also open possibilities for practical applications which could not be envisaged before. There has been an intensive research on the magnetocaloric response of superparamagnetic nanoparticles.^{11,12} More recently, it has been shown that the adequate control of the magnetic anisotropy of a nanostructured system can originate behaviors that are qualitatively different from those of the bulk materials.¹³ There have been studies of the influence on the MCE of the control of the anisotropy of the material, especially through surface modification processes, either by ball-milling zinc ferrite particles,¹⁴ which lead to disorder on the surface of the particles causing some of the ions to change from spinel to the inverse spinel structure, or by systems of core-shell nanoparticles,¹⁵ where the total magnetization of each particle may be considered as consisting of two parts: the core magnetic moment (which is ordered and behaves as a superspin) and the shell magnetization (which is mostly disordered and somewhat similar to spin-glass systems). The exchange coupling between the surface and core spins can lead to short-range order of the surface spins below a certain temperature with the surface anisotropy also competing in this process. This surface anisotropy that these particles exhibit at low temperatures causes the ΔS_M values obtained for these core-shell nanoparticles at their associated spin freezing transition to be the largest reported on any nanoparticle system so far.¹⁵ This transition, detected in the magnetization curves as an abrupt change in temperature dependence of magnetization, can be perceived as an order-disorder transition. While the critical characteristics of this phase transition cannot be studied using standard procedures such as the Kouvel–Fisher method, the analysis of the field dependence of MCE proposed recently by us is believed to be a useful tool for this purpose.¹⁶

In this work, we will show that the study of MCE of Co, Co–Ag, and Ni–Ag core-shell nanoparticles can give us additional information about the characteristics of that phase

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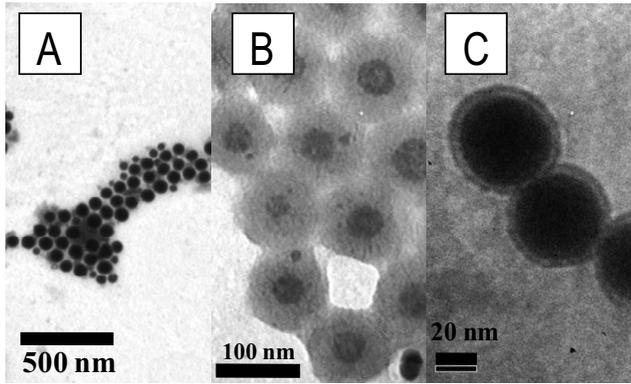


FIG. 1. Transmission electron micrographs of the nanoparticles (a) Co, (b) $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$, and (c) $\text{Ni}_{\text{core}}\text{Ag}_{\text{shell}}$.

transition. These different samples involve two different synthetic strategies based on the idea of forming core-shell structures. In the first approach, the passivating organic surfactant layer acts as the shell and monodisperse cobalt particles constitute the core thereby increasing the active magnetocaloric content and also decreasing the effective mass of the nanocomposite. In the second approach, a conductive shell in the form of Ag is used, with Co or Ni as the magnetic core. The presence of Ag not only provides a desirable high thermal conducting surface (beneficial for heat transfer to the lattice in practical refrigerator design) but also prevents agglomeration and surface oxidation that tend to degrade the magnetic and MCE properties of the composite.

Synthesis of monodisperse Co and Ni nanoparticles was performed by a simple, aqueous medium based wet chemical technique at ambient temperature with optimized concentration of a mixture of surfactants—sodium dodecyl sulfate and oleic acid.¹⁷ The $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$ and $\text{Ni}_{\text{core}}\text{Ag}_{\text{shell}}$ particles were synthesized by replacing the surface layer of Co and Ni nanoparticles with Ag using the transmetallation reaction.¹⁸ The particle morphologies were probed by transmission electron microscopy (Fig. 1). Magnetic characterization was done using a commercial 7 T physical property measurement system from Quantum Design. For the temperature- and field-dependent magnetization measurements, dried samples in powder form were packed into a gel cap and care was taken to enclose them tightly so that no mechanical motion of particles was possible under external fields. The details of the magnetic characterization of these samples, including the collection of the family of isothermal magnetization curves for extracting the MCE, have been reported in Ref. 15.

The MCE can be characterized by the magnetic entropy change due to the application of a magnetic field H , which can be evaluated from the processing of the temperature and field dependent magnetization curves using a numerical approximation to the equation,

$$\Delta S_M = \int_0^{H_{\text{max}}} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

where the partial derivative is replaced by finite differences and the integration is performed numerically.

The phenomenological universal curve is constructed by normalizing the magnetic entropy change curves with respect

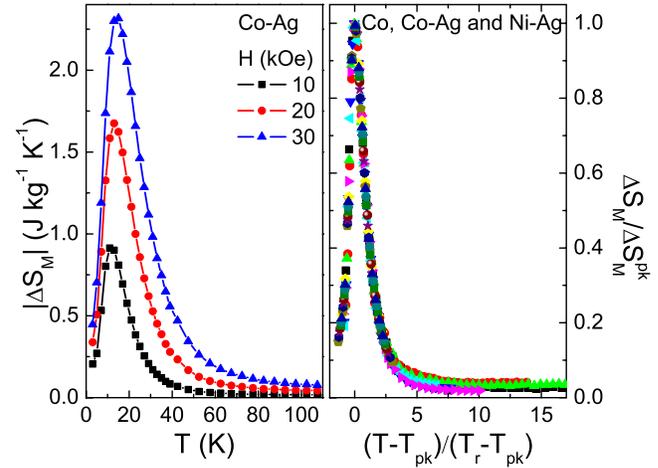


FIG. 2. (Color online) Left panel: Temperature dependence of the magnetic entropy change of the Co–Ag nanoparticles measured up to different maximum applied fields. Right panel: Collapse of the magnetic entropy change curves of all the studied samples onto a single universal curve.

to their peak, ΔS_M^{pk} , and rescaling the temperature axis⁶ using a reference temperature,¹⁹ T_r , [the one corresponding to $\Delta S_M(T_r) = 0.5\Delta S_M^{pk}$],

$$\theta = (T - T_C)/(T_r - T_C), \quad (2)$$

where T_C is the transition temperature. In the present study, we are not dealing with a Curie temperature but rather with a surface spin freezing temperature, so the transition temperature has been identified as the temperature of the peak entropy change, T_{pk} .

The upper panel of Fig. 2 shows the temperature dependence of the magnetic entropy change for different values of the maximum applied magnetic field for the Co–Ag core-shell nanoparticles. When these data are processed to construct the universal curve, they collapse onto a single curve, as shown in the lower panel of Fig. 2. This collapse of the ΔS_M curves has been found for the case of magnetocaloric materials with a second order phase transition^{6–10} and is therefore expected for the case of the core/shell nanoparticles as the surface spin freezing transition is typically an order-disorder transition. More remarkable is the collapse of the ΔS_M curves of the different Co, Co–Ag, and Ni–Ag samples. This implies that the critical exponents associated to this transition in the different studied samples should be equal, within the experimental error margin.

The surface anisotropy in nanoparticles is largely affected by the chemical as well as physical environment surrounding the particles. The surface magnetic properties may change under the influence of interparticle magnetic interactions as well as intraparticle exchange interaction between the core and shell regions.²⁰ Thus the overall change in the surface magnetic properties is most likely driven by the competition between intra- and interparticle interactions. At lower temperatures, the spins are frozen in the directions determined by these competing interactions as well as the effective anisotropy energy.

For the Co core-shell nanoparticles, Co nanocrystals are separated by the organic surfactant layer. In the other two cases, it is the Ag layer that separates the magnetic particles.

While the surface spin disorder in Co and Ni nanoparticles with just an organic surfactant coating is expected to be present, the ordering of the interfacial spins and the spin freezing characteristics are expected to be considerably altered with the presence of nonmagnetic metallic interfaces such as Ag. The configuration of interfacial spins is decided by the disorder (which will be different for the organic surfactant coating and for the metal shell layer) at the surface. This is generally influenced by several factors such as random anisotropy, broken bonds, and associated surface charge distributions and possible charge transfer across the interface.

The change in composition of the particles and nature of the shell can be used to tailor the magnitude and position of the peak,¹⁵ but the present results indicate that it does not alter the characteristics of the phase transition, as evidenced by the collapse of the ΔS_M curves.

The low temperature at which the transition takes place, together with the fact that there is another magnetic transition (the superparamagnetic/blocking transition of the core spins) at higher temperatures, prevents an accurate determination of the critical exponents from the magnetization curves, which could be used to compare the similarities of the spin freezing transitions of the studied samples. Nevertheless, taking into account that the magnetic entropy change has a peak at the surface spin freezing temperature and that its width is smaller than the distance to the superparamagnetic transition (i.e., the peaks corresponding to these two different magnetic transitions are not overlapped), the study of the field dependence of the magnetic entropy change peak can be used to qualitatively compare the transitions of the different samples.

It has been recently shown experimentally¹⁹ and demonstrated theoretically⁷ that there is a scaling law for the refrigerant capacity (RC) for materials with a second order phase transition,

$$RC \propto H^{1+1/\delta}. \quad (3)$$

Therefore, if the critical exponents characterizing the spin freezing transition are the same, the field dependence of RC for all these alloys should be the same and characterized by a single exponent. To test this feature, a nonlinear fit of RC versus field for the Ni–Ag sample measured up to 70 kOe has been performed to extract the value of the exponent in Eq. (3). That experimentally determined exponent value has been used to construct the abscissa axis of Fig. 3 and the RC data for the other samples have been plotted versus this axis. It is shown that, as expected, the behavior for all the data is linear, which hints again at an independence of the characteristics of the spin freezing transition with the nature of the shell.

In conclusion, the magnetocaloric peak of the spin freezing transition of Co, Co–Ag, and Ni–Ag core-shell nanoparticles has been studied under the point of view of the universal curve for the magnetic entropy change. It is shown that all the experimental data collapse onto the same universal curve, indicating that the nature of the phase transition is not altered by the characteristics of the shell (either organic sur-

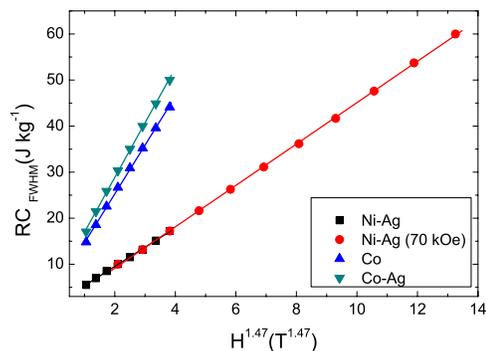


FIG. 3. (Color online) Field dependence of the RC (calculated as the product of the peak entropy change times the full width at half maximum of the peak) for the different studied samples. Lines are linear fits to the data. The exponent of the abscissa has been selected from the power law fit of the Ni–Ag (70 kOe) data.

factant layer of metallic Ag). This is confirmed by the scaling law of the RC of these samples.

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