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Scaling Analysis of the Magnetocaloric Effect in Co/Au Nanoparticles

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The system of superparamagnetic Co/Au bimetallic nanoparticles of average diameter 7 nm was investigated with respect to its magnetocaloric properties. DC magnetic measurements revealed the presence of field dependent zero field cooled $M(T)$ maximum (6–8 K) and significant zero field cooled/field cooled irreversibility at low temperatures in the system. Documented thermal hysteresis disallow standard magnetic entropy change calculation from isothermal $M(H)$ data, thus we attempted to employ zero field cooled $M(T)$ data for this purpose. Magnetic entropy change was calculated employing the Maxwell relation. In maximal field variation of 1 T relative high magnetic entropy change for nanoparticles $\Delta S_M \approx 0.7$ J/(kg K) at $T = 9$ K was observed. The data collapsed onto single universal curve after proper axis rescaling.

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1. Introduction

The magnetocaloric effect (MCE) is the adiabatic temperature change of a material upon application of a magnetic field. Since MCE can be utilized for magnetic refrigeration, suitable materials which could replace the conventional refrigerants have been investigated intensively. The observance of large MCE has been reported for several compounds [1, 2], however tuning the properties of bulk magnetic refrigerant for technical applications (generally by component doping) usually affect the crucial parameters in relative narrow interval of values. On the other hand, new progressive materials like nanoparticles (NPs) allow tailoring their characteristics significantly by controlling of their size, shape or capping layer. Moreover, the phenomena occurring in nanoparticle systems may differ completely from the phenomena characteristic of bulk materials. This hampers the application of standard theories and data analysis introduced for conventional materials in the sphere of nanostructures.

Number of works devoted to understanding of mechanism of MCE has been reported by now [3–5]. Among several methods for MCE evaluation that have already been proposed, the construction of universal curve is considered to be very interpretable. For the materials from the same universality class, magnetic entropy change dependence on temperature data obtained at different magnetic field changes should collapse onto one universal curve after proper rescaling. The shape and parameters of the master curve can provide us with information on the character of the phase transition or critical exponents [4, 6].

Thermal hysteresis (zero field cooled/field cooled (ZFC/FC) irreversibility at low temperatures) typical of superparamagnetic NPs is one of the features hindering direct application of common examination methods to nanoparticle systems. Standard data acquisition for MCE evaluation via magnetic entropy change, ΔS_M, is measuring isothermal magnetization, $M(H)$, from low to high temperatures [1, 2, 5]. However, it was demonstrated [7] that this procedure employed in materials with thermal hysteresis leads to unphysical ΔS_M calculations. The reason is that the memory of the sample was not erased in between measurements. One way how to eliminate this artifact is to record temperature dependent magnetization curves, $M(T)$, in constant magnetic field after heating the material high enough above the magnetic transition temperature. This is what ZFC protocol provides.

In this paper, we present the study of Co/Au bimetallic nanoparticle system with respect to its MCE properties. Since scaling analysis is unique tool providing the insight into the nature of $\Delta S_M(T)$ peak occurrence, we attempted to apply this method to our data. The collapse of the data onto single universal curve was observed.

2. Results and discussion

Investigated monodisperse Co/Au nanoparticle system was prepared by using the method of microemulsion. Average particle and magnetic Co core size $d \approx 7$ nm, $d_C \approx 5$ nm, respectively, was established. Details of synthesis, structural analysis and magnetic properties of the system have already been published elsewhere [8–10].

The magnetic properties measurements of the system were carried out by commercial device MPMS 5XL from Quantum Design. Isothermal magnetization curves were recorded in the interval 1.8–20.8 K with the step of

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0.5 K. The magnitude of maximal applied field was 5 T. ZFC/FC $M(T)$ data in temperature range 1.8–30 K were obtained in various applied magnetic field from 1 mT to 1 T.

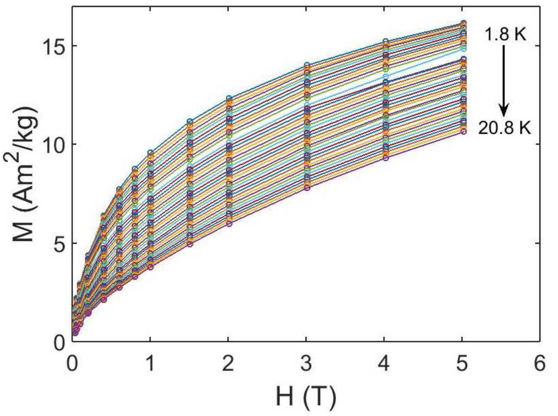

Fig. 1. Isothermal magnetization data of Co/Au nanoparticle system up to applied field of 5 T obtained at temperature range 1.8–20.8 K with the step of 0.5 K.

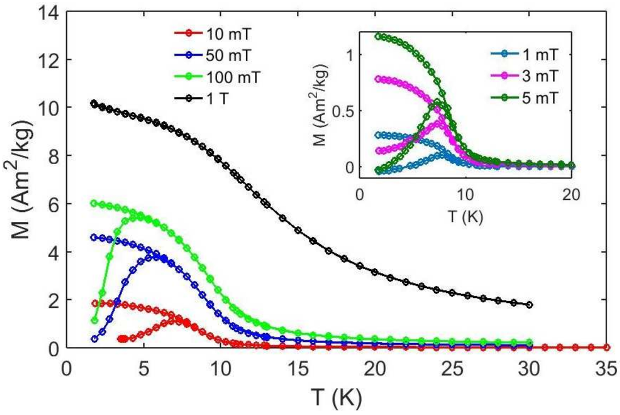

Fig. 2. ZFC/FC magnetization data of Co/Au nanoparticle system obtained at magnetic fields up to 1 T. Inset shows the magnification of the data obtained at three lowest applied magnetic fields 1, 3, and 5 mT.

Figure 1 presents the isothermal $M(H)$ curves of investigated Co/Au system with peculiar behavior in the vicinity of transition temperature 8 K. We attempted to process the data for magnetic entropy change calculation, however, numerous spikes emerged in $\Delta S_M(T)$ curves and subsequent universal curve construction failed. This could suggest on wrong protocol for data acquisition selection.

Figure 2 shows ZFC/FC magnetization vs. temperature data obtained at different magnitudes of applied magnetic fields. Features typical of superparamagnetic NPs have been recognized from the experimental data. The presence of maximum of ZFC curve and its shift towards lower temperatures with magnetic field increase is clearly evident. Further, high irreversibility of ZFC/FC curves at the temperatures lower than the temperature of corresponding ZFC $M(T)$ peak temperature documents significant thermal hysteresis of investigated system. Due to this, we did not follow standard protocol for data acquisition and instead of recording isothermal $M(H)$ curves at different temperatures, we utilized ZFC $M(T)$ data obtained at different applied fields for magnetic entropy change calculation.

Relationship between changes in magnetization and magnetic entropy can be expressed by the Maxwell relation [11] $(\partial M/\partial T)_H = (\partial S/\partial H)_T$, which for an isothermal-isobaric process after integration yields [5]:

$$\Delta S_M = \int \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H. \qquad (1)$$

For the discrete measurements there is a suitable approximation of Eq. (1) [1]:

$$\Delta S_M\left(\frac{T_{n+1}+T_n}{2}, H\right) = \sum \frac{(M_{n+1}-M_n)_H}{T_{n+1}-T_n}\Delta H, \qquad (2)$$

where M_n and M_{n+1} are the magnetization values measured in magnetic field H at temperatures T_n and T_{n+1}, respectively.

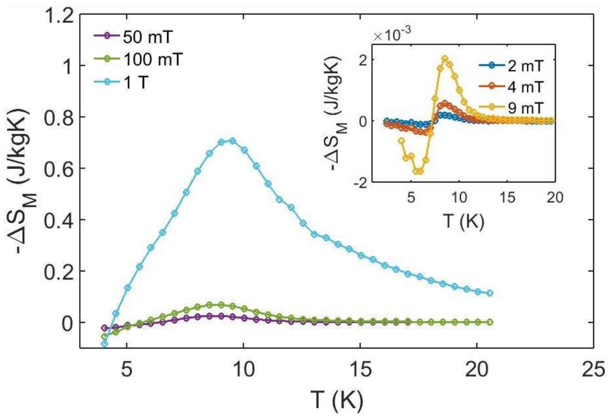

Fig. 3. Magnetic entropy change vs. temperature dependences of Co/Au NPs for the applied field variations from 2 mT to 999 mT. Inset is the magnification of the data corresponding to the three $\Delta S_M(T)$ curves calculated for lowest field changes 2.4 and 9 mT.

Figure 3 demonstrates $\Delta S_M(T)$ dependences for different field variations. Apparently, $-\Delta S_M(T)$ curves exhibit maximum at the temperature in the vicinity of ZFC $M(T)$ peak temperature. Gradual enhancement of $-\Delta S_M$ with the increase of magnetic field change is also evident in Fig. 3. Since $\Delta S_M(T)$ peak could be related to magnetic phase transition [2, 4], we attempted to apply scaling analysis developed for the second order phase transition (SOPT) in bulk materials to our Co/Au nanoparticle system.

According to Franco et al. [4, 6], there is a phenomenological universal curve for the materials with SOPT, onto which $\Delta S_M(T)$ curves should collapse after proper axis rescaling. At first, $\Delta S_M(T)$ data are normalized with respect to the their peak values ΔS_M^{pk}. Subsequently, temperature axis has to be rescaled below and above the

$\Delta S_M(T)$ peak temperature, T_p, according to Eq. (3) [4]:

$$\theta = \begin{cases} -(T - T_p)/(T_{r1} - T_p); & T \le T_p, \\ (T - T_p)/(T_{r2} - T_p); & T > T_p, \end{cases} \quad (3)$$

where T_{r1} and T_{r2} are the temperatures of the two reference points. These can be selected from the temperatures corresponding to $\Delta S_M(T_r, H_{\max})/\Delta S_M^{pk}(H_{\max}) = \alpha$, where α is a real number arbitrary chosen between 0 and 1. For this study, $\alpha = 0.5$ has been selected and the rescaled data are displayed in Fig. 4.

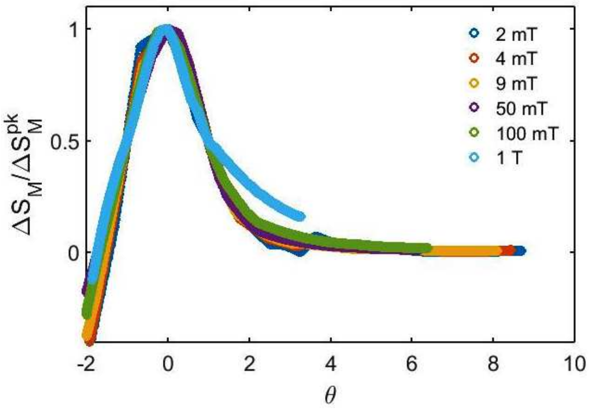

Fig. 4. Collapse of $\Delta S_M(T)$ data onto single universal curve.

After processing of the $\Delta S_M(T)$ data, collapse onto single universal curve can be observed. This could indicate that studied Co/Au nanoparticle system undergoes SOPT at the temperature corresponding to ZFC $M(T)$ maximum. Similar behavior has been revealed by Franco et al. [6] in the Co/Ag nanoparticle system. However, the presence of superspin glass state instead of spin glass state has been documented in our system at low temperatures [8], thus further complementary measurements and data analysis is necessary to perform in order to verify the presence of the SOPT in studied Co/Au system. Nevertheless, the applicability of scaling analysis to nanoparticle system has been demonstrated and behavior resembling the spin glass transition was revealed in examined Co/Au nanoparticles.

3. Conclusions

We have investigated Co/Au nanoparticle system with respect to its magnetocaloric properties. Since ZFC/FC measurements revealed significant thermal hysteresis of the system at low temperatures, we used ZFC $M(T)$ data instead of commonly used isothermal $M(H)$ data for magnetic entropy change calculations. In maximal field variation of 1 T relative high magnetic entropy for NPs $\Delta S_M \approx 0.7$ J/(kg K) at $T = 9$ K was observed. According to results presented in this work, $\Delta S_M(T)$ curves obtained for field variations from 2 mT to 999 mT collapsed onto single universal curve suggesting that the system could undergo second order phase transition at the temperature of ZFC/FC $M(T)$ irreversibility.

Acknowledgments

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References

[1] S. Ma, W.F. Li, D. Li, D.K. Xiong, N.K. Sun, D.Y. Geng, W. Liu, Z.D. Zhang, *Phys. Rev. B* **76**, 144404 (2007).

[2] P. Poddar, S. Srinath, J. Gass, B.L.V. Prasad, H. Srikanth, *J. Phys. Chem. C* **111**, 14060 (2007).

[3] R.D. McMichael, R.D. Shull, L.J. Swartzendruber, L.H. Bennett, R.E. Watson, *J. Magn. Magn. Mater.* **111**, 29 (1992).

[4] V. Franco, A. Conde, *Int. J. Refrig.* **33**, 465 (2010).

[5] V.K. Pecharsky, K.A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).

[6] V. Franco, A. Conde, D. Sidhaye, B.L.V. Prasad, P. Poddar, S. Srinath, M.H. Phan, H. Srikanth, *J. Appl. Phys.* **107**, 09A902 (2010).

[7] A.M.G. Carvalho, A.A. Coelho, P.J. von Rankhe, C.S. Alves, *J. Alloy Comp.* **509**, 3452 (2011).

[8] P. Hrubovčák, A. Zeleňáková, V. Zeleňák, J. Kováč, *J. Alloy Comp.* **649**, 104 (2015).

[9] P. Hrubovčák, A. Zeleňáková, V. Zeleňák, J. Kováč, *Acta Phys. Pol. A* **126**, 216 (2014).

[10] P. Hrubovčák, A. Zeleňáková, V. Zeleňák, J. Michalíková, *Solid State Phenom.* **233-234**, 497 (2015).

[11] H.B. Callen, *Thermodynamics*, Wiley, New York 1981.