Surface spin-glass, large surface anisotropy, and depression of magnetocaloric effect in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ nanoparticles

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The surface magnetic behavior of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ nanoparticles was investigated. We observed irreversibility in high magnetic field. The surface spin-glass behavior as well as the high-field irreversibility is suppressed by increasing particle size while the freezing temperature T_F does not change with particle size. The enhanced coercivity has been observed in the particles and we attributed it to the large surface anisotropy. We have disclosed a clear relationship between the particle size, the thickness of the shell, and the saturation magnetization of the particles. The large reduction of the saturation magnetization of the samples is found to be induced by the increase of nonmagnetic surface large since the thickness of the spin-disordered surface layer increases with a decrease in the particle size. Due to the reduction of the magnetization, the magnetocaloric effect (MCE) has been reduced by the decreased particle size since the nonmagnetic surface contributes little to the MCE. Based on the core-shell structure, large relative cooling powers RCP(s) of 180 J/kg and 471 J/kg were predicted for a field change of 2.0 T and 4.5 T, respectively, in the small particles with thin spin-glass layer. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768842>]

I. INTRODUCTION

The physics of nanoscale magnetic materials have been studied vividly in recent years, not only from the fundamental research point of view but also for technological reasons.^{1–4} When the size of the magnetic particles decreases to a few nanometers, magnetic particles become single domain in contrast with the bulk magnetic materials and exhibit a number of outstanding physical properties such as superparamagnetism (SPM),⁵ super-spin-glass,⁶ surface spin-glass, and quantum tunneling of the magnetization.^{7,8} In nanoscale magnetic materials, the symmetry breaking at the surface results in a surface anisotropy. In most cases, surface anisotropy is strong enough to compete with the exchange energy that favors full alignment. It is understandable that the magnetization vector points along the particle anisotropy axis in the core of the particle, turning gradually into a different direction when it approaches the surface. Therefore, the magnetization near the surface is generally lower than that inside the nanoparticles, inducing the reduction of the saturation magnetization M_s .⁹ The reduction of M_s was intensively investigated in the past decades since it was found by Berkowitz *et al.*¹⁰ However, the problem is still in debate with arguments in favor of a surface origin^{11,12} and in favor of a finite size effect.^{13,14} Some examples of surface disorder can be found in ball-milled CoFe_2O_4 ,¹⁵ NiFe_2O_4 .^{16,17} According to these results, a core-shell type structure can be proposed that the core is ferromagnetic (FM) while the shell is spin-disordered.^{18,19} For the doped perovskite manganites which are well-known as colossal magnetoresistance (CMR)

materials, the surface disorder may also evidenced by the observation of surface phonon.²⁰

In our previous work, we have evidenced the coexistence of SPM, superspin-glass (SSG) and surface spin-glass in the $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LCMO) nanoparticles according to de Almeida-Thouless (AT) line fitting.²¹ The core-shell model was found suitable for discussing the magnetic behavior of our sample. The magnetic properties especially the magnetocaloric effect (MCE) can be greatly modified through the change of the particle size. The entropy change of the fine particles (for example, the 17 nm sample) is very low and the RCP is also very low although it has the broadened full-width of half maximum of entropy change. The cause of depressed magnetocaloric effect is still unclear. In this paper, we confirm the existence of a spin-glass-like surface layer by the observation of the high field irreversibility in the $M(H)$ curve, and attribute the reduction of M_s as well as the MCE to the increased thickness of the surface spin-glass shell. If the thickness of the surface layer can be reduced, the MCE will be increased greatly.

II. EXPERIMENT

The sample was prepared using the sol-gel method.²¹ X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation (Philips X'pertPro) was used to determine the crystal structure, lattice parameters, and crystallite sizes. XRD patterns were analyzed by the Rietveld method. The magnetization measurements were carried out by using a Quantum Design superconducting quantum interference device (SQUID). The surface morphology of the samples was studied by field-emission scanning electronic microscopy (FE-SEM).

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III. RESULTS AND DISCUSSION

The XRD patterns of nanocrystalline $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ particles were shown in Fig. 1 in Ref. 21. The average crystallite sizes D are calculated by using the Scherrer formulation $D = k\lambda/\beta(\cos 2\theta)$, where D is the diameter of the particle, k is a constant (0.9), λ is the wavelength of the x-ray, β is the full width of the half maximum of a peak, and θ is the Bragg angle. The particle size is about 17 nm, 19.5 nm, 28 nm, 35.5 nm, and 43 nm, respectively, for different annealing temperatures. The SEM graph confirmed the calculated size generally. All the samples can be indexed by orthorhombic setting of the $Pnma$ space group and no secondary phases can be found. Figure 1 shows X-ray diffraction pattern and Rietveld refinement result for 17 nm (annealed at 600 °C for 8 h) sample at room temperature. We can see that the diffraction peaks are very broad, indicating that grain size is small in this sample. Although it is annealed at low temperature of 600 °C, all diffraction peaks can still be indexed by the orthorhombic setting of the $Pnma$ space group and no detectable secondary phases can be found in this sample as shown in Fig. 1. The results of Rietveld refinements of our samples are shown in Table I. We also obtain a sample with particle size about 15 nm, annealed two times at 600 °C for 3 h.

Figure 2 presents the temperature dependence of the dc magnetization under zero-field-cooled (ZFC) and field-cooled (FC) processes with an applied field of 0.01 T for the 17 nm sample. The ZFC magnetization exhibits a maximum at 83 K, while the ZFC and FC curves begin to diverge at 218 K well above the temperature corresponding to the maximum magnetization. Both of the two characteristics indicate the SPM behavior existing in these samples. A more interesting feature is that the FC curve reveals the existence of a sudden increase in magnetization below $T_F = 43$ K (this characteristic is much clear in an enlarged curve of the FC process in the inset of Fig. 2) which is considered to be the onset of the freezing temperature of the surface spin-glass layer.⁴ A similar feature of spin-glass can also be seen in Fe_2O_3 and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles and such spin-glass-like behavior is denoted as a surface effect.^{4,22} According to fitting AT line to the H dependence of peak temperature of the ZFC magnetization, different parameters are derived. These data indicate the coexistence of SPM, SSG, and surface spin-glass in the fine

FIG. 1. X-ray diffraction pattern (crosses) and Rietveld refinement result (solid curve) for 17 nm $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ sample at room temperature. The difference between the data and the calculation is shown at the bottom. The goodness parameters of refinement are indicated.

TABLE I. Results of Rietveld refinements in orthorhombic setting of the $Pnma$ space group determined from XRD patterns measured at room temperature for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ nanoparticles.

T_{anneal} (°C)	D (nm)	a (Å)	b (Å)	c (Å)	R_p (%)	R_{wp} (%)	χ^2 (%)
600	17	5.4619	7.7252	5.4973	7.481	9.770	1.522
700	19.5	5.4595	7.7271	5.4921	7.212	9.282	1.354
800	28	5.4694	7.7552	5.4905	7.352	9.602	1.361
900	35.5	5.4678	7.7627	5.4945	7.813	10.131	1.354
1000	43	5.4785	7.7481	5.5032	7.108	9.506	1.317

FIG. 2. Low field ZFC-FC magnetization of nanosized $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ showing the blocking process of the particles at $T_B = 83$ K. Inset: Detail of the FC branch showing the sudden increase of the magnetization at about 43 K.

particles. Especially, the fitting data show a very large surface isotropy field of $H_a = 48.8$ T indicating the large surface anisotropy.²¹

To confirm the magnetic behavior of the samples, we measured hysteresis loop of the samples at the temperature of 5 K. Figure 3 shows the first quadrant of magnetization hysteresis loop of 17 nm sample. We found the divergence of the $M(H)$ curve in high field region, indicating that the irreversibility exists in the field as large as 4.5 T. Our interpretation is that the open hysteresis loop at high field is the result of irreversible changes between the surface spin configuration rather than reversals of particle as whole since the magnetic anisotropy of LCMO is very low; the full alignment of

FIG. 3. Detail of the isotherm $M-H$ curve of 17 nm sample measured at 5 K. Inset: temperature dependence of the DC magnetization via zero-field-cooled processes with an applied field of 4.5 T.

the spins can be reached in a field much lower than 4.5 T. We can also see that the magnetization is far from saturation, at the field of 4.5 T. These results may confirm our fitting data of extremely large H_a value. The inset of Figure 3 shows $M(T)$ curve via ZFC process with an applied field of 4.5 T. The magnetization maximum can be found at about 20 K in this curve, indicating that the irreversibility has not been suppressed in the field of 4.5 T. This curve is accordance with irreversibility at high field in hysteresis loop. The large irreversibility in high field is the characteristic of surface spin-glass which induced by the spin-disorder of the surface layer and large surface antistrophic field.⁴ According to the discussion above, we conclude that for our LCMO samples, the surface spin-glass indeed exists.

Figure 4 shows the grain size dependence of $M(T)$ magnetization of FC procedure for LCMO samples. For 15, 17, and 19.5 nm samples, the sudden increase in magnetization can be seen and the sudden increase becomes unclear as particle size increases. For the particles larger than 19.5 nm, the increases can hardly be observed. We attribute this result to the reduction of the number of surface atoms which can be ignored compared with atoms in core in larger particles; thus, the surface-spin-glass behavior cannot be detected. On the other hand, we find that the freezing temperatures T_F are 43 K for all the samples though the spin-glass behavior is weakened. The invariant of T_F with particle size indicates that the exchange interaction in the surface layer remains constant and independent with particle size.

Figure 5(a) shows the isotherm magnetization curves $M(H)$ at 5 K for samples with different sizes. We can see hysteresis in high field region for the samples with small particle sizes while for the larger ones the hysteresis nearly vanishes, indicating that the high-field irreversibility is sensitive to the particle size. This reduction of the high field irreversibility also indicates the reduction of surface layer with the increase in particle size. Figure 5(b) shows the isotherm magnetization curves in the low field region. It can be seen that the coercivity H_C increases as particle size decreases as shown in the inset of Fig. 5(b). It is well-known that sufficiently small magnetic particles are usually single domains, with atomic spins completely aligned by exchange interactions. The rotational barriers due to magnetocrystalline, magnetoe-

FIG. 4. The size dependence of low-field $M(T)$ curves via FC processes for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$. Inset: the first derivative of $M(T)$ curve in FC model for the 15, 17, and 19.5 nm samples.

FIG. 5. (a) Isotherm magnetization curves $M(H)$ at 5 K for samples with different particle sizes; (b) the isotherm magnetization curves in the low field region and the inset shows size dependence of H_C .

lastic, and shape anisotropy can trap particles in two or more metastable orientations, giving rise to hysteresis. In an ideal monodisperse system, a single magnetic domain should be expected for manganite particles with a size lower than a critical value of $D_C = 70$ nm.²³ Although our real system is polydisperse in nature, the reasonably narrow distribution of particle sizes, especially for the $D = 15, 17, 19.5$, and 28 nm samples indicates that the maximum particle size is not expected to cross 70 nm. Thus, we can assign the nature of the physical structure of these samples as assemblies of single domain particles. Thus, SPM should be expected in these single domain systems. H_C of the SPM particles should increase with increasing particle size, since the sample magnetized through the rotation of the magnetic moment of the particle as a whole.^{24,25} On the other hand, the large spin in the ferromagnetic core may result in dipole-dipole interaction; hence, the super-spin-glass can also be induced.^{21,25} This also results in the irreversibility of the particles. Since the larger volume of the particle, the dipole-dipole interaction and the anisotropy in the large particles can be larger than that in small particles. Thus, the larger magnetic field should be needed to overcome the increased anisotropic energy in large particles. However, in our samples H_C decreases with increasing particle size, which seems contradict with the single domain and the super-spin-glass model. If the surface effect was considered, this contradiction should be eliminated. For our samples since the particles are small, the anisotropy of the spin-glass layer should never be ignored. Thus, the effective magnetic anisotropic energy E_A which dominates the coercivity should be composed of three parts: the effective magnetic anisotropic energy of the core

(E_A^c), the super-spin-glass induced anisotropic energy E_A^d , and the effective magnetic anisotropic energy of the surface (E_A^s). If we assume that the particles are sphere, E_A^c and E_A^s should be expressed as

$$E_A^c = K_c V_c = \frac{1}{6} \pi K_c (D - 2t)^3$$

$$= \frac{1}{6} \pi K_c (D^3 - 6D^2t + 12Dt^2 + 8t^3), \quad (1)$$

$$E_A^s = K_s V_s = \frac{1}{6} \pi K_s (D^3 - (D - 2t)^3)$$

$$= \frac{1}{6} \pi K_s (6D^2t - 12Dt^2 - 8t^3), \quad (2)$$

where K_c and K_s are the effective anisotropic constants of the core and the shell, respectively; and V_c and V_s are the volumes of the core and the shell, respectively. As for the super-spin-glass induced anisotropic constant K_d , it is much smaller than K_s but larger than K_c as derived later. Therefore, E_A can be expressed as

$$E_A = \frac{1}{6} \pi (K_c + K_d) (D^3 - 6D^2t + 12Dt^2 + 4t^3)$$

$$+ \frac{1}{6} \pi K_s (6D^2t - 12Dt^2 - 8t^3).$$

Dividing the whole volume of the particle, the effective anisotropic constant should be $K = (K_c + K_d)(1 - \frac{6t}{D} + \frac{12t^2}{D^2} + \frac{8t^3}{D^3}) + K_s(\frac{6t}{D} - \frac{12t^2}{D^2} - \frac{8t^3}{D^3})$. Using our fitting data of H_a in Ref. 21, $K_c = 1.48 \times 10^4$ J/m³, $K_d = 4.48 \times 10^4$ J/m³, and $K_s = 7.54 \times 10^6$ J/m³ can be calculated in our 17 nm sample using $KV = \mu H_a$, where μ is the effective moment of our LCMO ($3.86 \mu_B$). We can see that K_c and K_d in the core are about hundred times smaller than K_s in the surface. Dropping high order terms, Eq. (2) can be expressed

$$K = K_c + K_d + K_s \frac{6t}{D}. \quad (3)$$

If the dipole-dipole interaction can be ignored, and letting $K_s t = K_s'$, thus K_s' denotes the anisotropy energy per area, effective anisotropy constant can be expressed as $K = K_c + \frac{6}{D} K_s'$, which is the same as that in other article.^{25,26} In our samples, the thickness of the surface layer is comparable to the particle size since the particle size is small. Therefore, the effective anisotropic constant increases dramatically as the particle size decreases. Thus, H_c increases with the decreased particle size which is accordance with our experimental result.

From Fig. 5(a) we can also see that for the 43 nm sample, the magnetization saturates in a relatively low field, and M_s nearly reaches the value for full alignment of the Mn spins ($3.86 \mu_B/\text{f.u.}$), while for the 17, 19.5, and 28 nm samples the magnetization is very low compared with the bulk value. The magnetizations of these samples increase slowly with applied field in high field and do not reach saturation in 4.5 T. Based on the core-shell structure, the inner part of the particle, i.e., the core, would have ferromagnetism while the outer layer, i.e., the shell, would contain most of the oxygen

defects and imperfection in the crystallographic structure, which would lead to a magnetically dead layer; thus, the surface atoms contribute very few magnetic moment on M_s of the nanosized particles. When magnetic field was applied, the magnetic core saturates easily while the magnetization of spin-disordered shell increases linearly with H after the linear contribution ($M = \chi H$).²⁷ The magnetization of the core can easily be derived by subtracting this linear contribution.

Fig. 6 shows the saturation magnetization of the core of 17, 19.5, 28, 35.5, and 43 nm samples. The saturation magnetization was derived by linearly extrapolating the initial magnetization isotherms $M(H)$ to 0 T from the high magnetic field larger than 2 T. The inset of Fig. 6 shows the magnetization of the magnetic core after the linear contribution of the shell was subtracted. We can see that the saturation magnetization of the 17 nm sample is $1.03 \mu_B/\text{f.u.}$ (about 3.75 times smaller than the saturation magnetization of $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ bulk material), indicating that the content of the nonmagnetic surface layer is very large. If we assume that the surface layer is only 1 nm as reported in other paper,²⁸ for 17 nm sample, the M_s should be about $3.2 \mu_B/\text{f.u.}$ much larger than our measured value of $1.03 \mu_B/\text{f.u.}$ Thus, the thickness of the nonmagnetic shell should be much larger than 1 nm. Inset (a) of Fig. 6 shows the magnetization of the initial $M(H)$ curves of the core and the whole samples. It is worth mentioning here that linear extrapolating the curve of $M(H)$ to the higher field we find that the magnetization will reach the bulk value at 41.6 T for 17 nm sample. This large value is close to the A-T line fitting value of $H_a = 48.8$ T and also accordance with the fact that the saturation has not been reached even in the field as high as 47 T in nanosized $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanoparticles.²⁹ Thus, it may indicate that both the core shell structure and A-T line fitting are correct and surface anisotropy of our LCMO nanoparticle is indeed very large.

Based on discussion above, the thickness of the surface layer can be derived. For the nanoparticle, the saturation magnetization of the core is decided by the ratio of its content thus can be described by $M_s = M_{s0}(D - 2t)^3/D^3$, where

FIG. 6. Size dependence of saturation magnetization M_s at 5 K. Inset: (a) the initial magnetization isotherms $M(H)$ of the magnetic core, and the dashed curves are the measured magnetization of LCMO samples of 17 nm, 19.5 nm, 28 nm, 35.5 nm, and 43 nm, respectively. (b) The size dependence of the shell thickness t . Black solid squares derived from saturation magnetization of the FM core, and the red solid circle are derived from the slope of the $M(H)$ curve of the nonmagnetic shell. Solid curves guide to eye.

M_{s0} is the saturation magnetization of the bulk material ($3.86 \mu_B/\text{f.u.}$), D is the particle size, and t is the thickness of the shell. Inset (b) of Figure 6 shows the estimated thickness t (black solid square). We can see that the thickness of the nonmagnetic shell increases with the decrease in particle size. For 17 nm sample, the thickness of the shell is about 3.0 nm while for the 43 nm sample t is only about 0.1 nm.

The thickness t can also be estimated by the magnetization of the nonmagnetic shell directly if we assume that the slopes of the magnetization lines of the non-magnetic shells are proportional to the volume content of the shells, i.e., $k_1/k_2 = D_1^3 - (D_1 - 2t_1)^3 / D_2^3 - (D_2 - 2t_2)^3$ where k is the slope of the magnetization line of the surface layer dividing the whole volume of the particle. Letting $t_2 = 3.0$ nm as have been derived by the saturation magnetization, other magnetization can be calculated by the equation. The derived t is shown in the inset of Fig. 6(b) (red solid circle). These data comply with the saturation magnetization derived value. Thus, we can conclude that t indeed increases as particle size decreases. For the sample of 17 nm, about 70% atoms are in the nonmagnetic surface layer according to our calculation. Therefore, we can conclude that the surface spin-glass can be enhanced and the magnetization is decreased dramatically by decreasing the particle size.

To explain the magnetic surface spin-glass behavior of our samples, the characteristic of the double exchange mechanism should be considered. For mixed-valence manganites, the ferromagnetism is induced by the hopping of the e_g electrons from the Mn^{3+} ion to neighboring Mn^{4+} , which tends to align the localized t_{2g} spins ferromagnetically through Hund's rule coupling. The hopping of the e_g electron depends on the degeneracy of the $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$ and $\text{Mn}^{4+}\text{-O}^{2-}\text{-Mn}^{3+}$ state.³⁰ Therefore, the high symmetry should be critical for the double exchange. While for the atoms near the surface the symmetry was broken since half of the bonds of surface atoms are vacant, and the Madelung potential near the surface is very different from that in the core. Therefore, the e_g electrons were localized near the surface hence double exchange was destroyed. For the magnates with localized e_g electron, the superexchange interactions may dominant interactions between Mn moments. The sign of superexchange depends on the valences of neighboring Mn ions.³¹⁻³³ For $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$ and the $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{3+}$ superexchange, the exchange integral is positive that is to say it is coupled ferromagnetically. On the other hand, for the $\text{Mn}^{4+}\text{-O}^{2-}\text{-Mn}^{4+}$ superexchange it coupled antiferromagnetically. Considering the Mn^{4+} and Mn^{3+} both existing in the mixed-valence manganites, these three interactions coexist. Thus, the coexistence of ferromagnetic interaction and antiferromagnetic interaction causes frustration, resulting in a spin-glass state in the surface layer.

Besides the surface induced break of symmetry, the vacancies near the surface may be another important factor results in the surface spin-glass. For our sol-gel and annealing preparation of LCMO sample, it is well known that the crystal is formed by the atom diffusion. The crystal nucleus formed first and grows from the core to outer layer; thus, the nucleus of the grain crystallizes well, while the outer layer of the grain crystallizes not as well as the core since they are

new formed; therefore, the diffusion action has not completed. Thus defects may be formed in the outer layer of the grain. These defects destroy the double exchange by destroying the hopping of the e_g electron since the local symmetry of the particle is destroyed; hence, superexchange becomes dominate the exchange interaction and frustration was induced. The defects induced surface spin-glass and reduction of the saturation magnetization have been observed in the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_x$ samples with various oxygen stoichiometries, and in radiation damaged $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ film.^{31,34} Meanwhile, the defects distribution is not evenly distributed. At the location approaching the core the defects are in low density and at the location approaching the surface, the defects are of high density. Thus, the gradient of the defect distribution intensifies the break of the symmetry. For samples annealed at low temperature, the surface layer with defects is thick since their low diffusing rate. That is why the spin-glass layer is so thick in the small particles. As we can see in Fig. 6 the spin-glass layer is about 3.0 nm and over 70% of the grain is the surface-spin-glass layer in our 17 nm sample.

Due to the increased content of surface spin-glass layer, the low magnetization and MCE may be induced. In our previous work, we find that the entropy change (ΔS_M) is very low in the fine particles (17 nm, for example) and the RCP is also very low although they have the broadened full-width of half maximum.²¹ The large content of the nonmagnetic surface layer may be the reason why the magnetization of fine particles is of such low value. The nonmagnetic surface layer contributes few MCE since its magnetization is very low and nearly independent of temperature (the $M(H)$ curves at different temperatures are nearly parallel to each other as shown in Fig. 6 of Ref. 21), indicating the magnetization of the shell is nearly independent on T . According to the equation^{35,36}

$$\Delta S_M = \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH, \quad (4)$$

we can see that the surface induced ΔS_M is nearly zero since M is nearly independent of T . Thus, ΔS_M and the peak width of ΔS_M are only decided by the transition of PM-FM transition and the superparamagnetism of the fine particles which only occurs in the magnetic core.²¹ Therefore, the surface layer may reduce the MCE as much as 70% in the 17 nm sample since the surface-spin-glass layer is more than 70% in content. ΔS_M of the sample is only 0.25 J/kg K and 0.62 J/kg K for field changes of 2.0 T and 4.5 T, respectively, and the RCPs are only 53.5 J/kg at 2.0 T and 137.0 J/kg at 4.5 T although it has the broad entropy change peaks.²¹ So it is reasonable to assume that if the surface effect can be eliminated the maximum entropy change of the sample can be raised dramatically. According to our estimation, 0.86 J/kg K and 2.13 J/kg K for field change of 2.0 T and 4.5 T can be derived if the shell thickness was reduced to 0.5 nm which is the typical shell thickness value usually in other systems⁴ (the magnetic core will be 91.5% in content). RCP of the 17 nm sample can be enhanced dramatically to 470 J/kg for field change of 4.5 T which is much larger than the maximum value of 348.6 J/kg in our 28 nm sample the largest

value derived in our samples. For a field change of 2.0 T, the RCP will be about 184 J/kg which is about 2 times more than that of the 43 nm or bulk sample. These RCP values are larger than all the representative magnetic refrigerant materials as far as we know.^{36,37} The large RCP value should be attainable in nanoparticles since the preparation of the nanoparticles with thin surface layer may be realizable from the technological point of view. Considering the advantages of perovskite manganites, such as high efficiency, good chemical stability, tunable ordering temperature by doping methods, higher electrical resistivity and low production costs, and these compounds could be the promising candidates for magnetic refrigeration.

IV. CONCLUSION

In summary, for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ nanoparticles, we have observed the existence of a low-temperature surface spin-glass layer that becomes frozen below $T_F = 43$ K. The large surface anisotropy constant was confirmed by the irreversibility in the $M(H)$ curve. The surface spin-glass as well as the irreversibility is weakened by the increase in particle size. However, T_F does not change with the particle size, indicating that the exchange integral does not change with particle. The coercivity increases with particle size due to the large anisotropy of the surface layer. The prominent reduction of saturation magnetization was found in our samples with small size which is due to the increased thickness of surface layer. It is also found that the thickness of non-magnetic surface layer increases with the decrease in particle size induced by the symmetry break induced by the surface effect and the defects in the surface layer. If the thickness of the surface layer can be reduced, the RCP of the LCMO nanoparticle will reach a very high value which is larger than that of magnetic refrigerant materials as far as we know and made these nanosized materials as the promising materials for the magnetic refrigeration.

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