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Particle size dependent hysteresis loss in $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ first-order systems

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Here, we report particle size dependent hysteresis loss in $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$. Hysteresis loss was getting smaller with reducing the particle size. The reduced ratio can be as high as ~61% as the sample is ground from bulk into small particles (20-50 μm). Such reduction can be ascribed to the notably increased surface area of sample and the partially removed internal strain and grain boundaries, other than nucleation factors and electronic band structure. Meanwhile, entropy change $|\Delta S|$ slightly decreases, but the effective refrigeration capacity shows an increase due to the notable reduction of hysteresis loss. Our investigations also reveal particle size limitation. When the size is below 10 μm (average ~ 4 μm), the sample may lose its stability and the $|\Delta S|$ notably reduces. © *2012 American Institute of Physics*. [doi:10.1063/1.3684244]

An increasing attention has been attracted to magnetic refrigeration technique because of environmental concerns and energy savings. The discovery of first-order magnetocaloric materials, i.e., $Gd_5Si_2Ge_2$, $MnFeP_{0.45}As_{0.55}$, $LaFe_{13-x}Si_x$, $MnAs_{1-x}Sb_x$, NiMnGa, and etc., stimulated high interest on practical applications in recent years.[1] Among these materials, $La(Fe,Si)_{13}$-based compounds with $NaZn_{13}$-type structure attract much attention due to easy preparation, cheap raw materials, and non-toxic characters.[2,3] Several demo-machines using $La(Fe,Si)_{13}$-based compounds as working substances have been tested and confirmed the excellent performance of the compounds.[4,5] However, a large hysteresis loss usually accompanies the magnetocaloric effect (MCE) due to the first-order nature of magnetic transition, which harms the refrigeration efficiency in magnetizing-demagnetizing cycling. Dynamic behaviors of first-order magnetic transitions have been studied for the typical MCE materials $LaFe_{11.7}Si_{1.3}$ and $Gd_5Si_2Ge_2$ by measuring magnetic relaxation, and the results were interpreted in terms of a thermal activation model.[6,7] The energy barrier in the model was expected to be connected with the electronic band structure, and the nucleation during transition could be induced by thermal activation. For $LaFe_{11.7}Si_{1.3}$, the critical nucleation size was found to be about 4.2 nm.[7]

Generally, the experimentally observed hysteresis in first-order systems correlates with intrinsic and extrinsic factors. Intrinsic ones usually include strain effect, frictions from domain rearrangements, impurity and nucleation factors, band structure, and etc. Extrinsic ones mainly refer to the thermal equilibrium and the situation of heat transfer during measurements, which directly relates to the deviation of temperature detector from sample, field/temperature rate, heat capacity and thermal conductivity of sample, surface area of sample to volume ratio, and etc. One knows that strong magnetic volume effect is a common feature for the first-order magnetocaloric materials. Strain effect and frictions from domain rearrangements are unavoidable. Moore *et al.*[8] studied Gd_5Ge_4 system and found that when the sample was broken into fragments with size ~100 μm, the operating field for transition became lower due to the reduction of internal strain. However, they found that when the sample was further ground into fine powder (particle size <100 μm), magnetic transition and MCE nearly disappear. They particularly studied extrinsic hysteresis in first-order La(Fe,Co,Si) systems and found the magnetic hysteresis is strongly sweep-rate dependent due to the reason of heat transfer. This deleterious effect can be greatly reduced by changing sample geometry or by using second-order materials.[9] Lyubina *et al.* studied the performance of LaFeSi system with porous architecture and found magnetic hysteresis can be improved due to partial removal of grain boundaries that restrain volume expansion, and excellent performance can be maintained.[10] However, at paramagnetic region of these porous alloys, the magnetization is still large and does not approach zero, which has been ascribed to the appearance of a large amount of α-Fe.

Detailed discussion on the size dependent hysteresis, particularly for the particles smaller than 100 μm, is still limited. People do not know whether there is any size limitation. For $La(Fe,Si)_{13}$-based MCE materials, $La(Fe,Si)_{13}H_\alpha$ hydrides were usually chosen to be room temperature refrigerants because their large MCE keeps nearly unchanged while shifting the transition temperature through controlling H content. To make sample homogenization with H atoms, particles smaller than 100 μm were often adopted to anneal in H_2 atmosphere.

Here, we report size dependent hysteresis loss and MCE for $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ first-order particles smaller than 120 μm. Our studies indicate that when the particle size is above 20 μm, the samples keep stable. Hysteresis loss is getting smaller while effective entropy change keeps nearly unchanged, and effective refrigeration capacity (RC) enhances with reducing particle size. However, as the particles are further ground into extra-fine powder (<10 μm, average

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$\sim$4 μm), samples lose their stability and the MCE remarkably reduces.

We prepared $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ bulk materials by conventional arc-melting technique. Subsequently, annealing was performed at 1080 °C for 30 days and then quenching in liquid nitrogen. Here, it is noteworthy that we adopt industrial La-Ce alloy (purity 99.0 wt. %, atomic ratio La:Ce = 1:1.88 similar to that in minerals) as starting materials. As known, the deposits of Ce, La on the earth are rich compared to other rare earth metals, and more importantly, these two co-exist with high ratio in many minerals. To purify La-Ce alloy with natural ratio is much easier compared to obtaining individual La or Ce; thus, the cost of industrial La-Ce alloy is lower than either La or Ce. During preparation, C was supplied by Fe-C alloy, and the lack of La was supplied by individual La. Besides La-Ce alloy, purities of Fe-C, La, and Si are 99.9 wt. %, 99.9 wt. %, and 99.91 wt. %, respectively. Our experiments manifested that the coexistence of impurities in the starting materials does not impair the formation of $NaZn_{13}$-type structure. Powder x-ray diffraction using Cu *K*a radiation indicated that the phase is clean for the C-doped samples.

The polycrystalline bulk $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ was ground into irregular particles by hand using an agate mortar, then the particles were separated into different size range using sieves as following, big size: 90-120 μm, middle size: 50-90 μm, small size: 20-50 μm, and fine powder: $<$10 μm ($\sim$4 μm in average). Meanwhile, an irregular single fragment (mass: 2.7 mg, size $<1\times1\times1$ mm) from the same ingot was chosen as bulk for comparison.

Magnetic measurements performed using SQUID-VSM (Superconducting Quantum Interference Device-Vibrating Sample Magnetometer) indicated that both Curie temperature T_C and saturated magnetization remain unchanged as the particle size is above 20 μm. Thermal magnetization measurements under 0.02 T indicated that the T_C, for the big (90-120 μm), middle (50-90 μm), and small (20-50 μm) particles, fixes at the same position, $\sim$200 K, compared to the bulk. This fact can be easily understandable because we do not believe any change of structure and bond length, and R-T (rare earth-transition), T-T (transition-transition) coupling took place as the sample changes from bulk to these particles. Fig. 1(a) displays magnetization isotherms on field increase and decrease in a wide temperature range covering T_C for these particles compared to the bulk. The field sweep rate is the same, 100 Oe/s, for all the measurements. Fig. 1(b) shows the deduced hysteresis loss (enclosed area in a field cycle) as a function of temperature for the corresponding samples. One can notice that the field-induced itinerant electronic metamagnetic (IEM) transition remains but becomes less sharp with reducing particle size; meanwhile, hysteresis loss is getting smaller. The maximal hysteresis loss remarkably reduces from 98.4 J/Kg at bulk to 38.8 J/Kg at particle size 20-50 μm. The reduced ratio is as high as $\sim$61%. These results suggest that breaking the materials into particles smaller than 120 μm is an effective way to reduce hysteresis loss while remaining the strong IEM transition behavior. Hysteresis effect is a complicated issue in the thermoelastic transformation system. The dissipative mechanisms are different at different spatial scales. At a microscopic scale, the hysteresis is related to the nucleation of phase. But at a mesoscopic scale, the hysteresis closely relates to the rearrangement of domains, frictions at grain boundaries, and situation of heat transfer. According to the studies on the dynamic behavior of first-order transitions based on thermal activation considerations, the energy barrier closely correlates with the electronic band structure, and the critical nucleation size is about 4.2 nm for $LaFe_{11.7}Si_{1.3}$.[7] As the particle size is above 20 μm, we do not think any change about nucleation factors related to physics origin takes place. So, the main reason for the observed hysteresis reduction should be the factors other than electronic band structure. In the typical first-order MCE systems, internal strain effect and frictions from domain rearrangements are inevitable due to the strong magnetic volume effect. Recent studies indicate that partial removal of internal strain and grain boundaries by altering sample geometry or introducing porous can reduce operating field[8] and improve MCE performance.[10] Moreover, a better situation of heat transfer can reduce extrinsic hysteresis.[9] If we suppose average size of the bulk, big (90-120 μm), middle (50-90 μm), and small particles (20-50 μm) is 945, 105, 70, and 35 μm, respectively, the surface area of sample to volume ratio can be roughly estimated to be 1:9:13.5:27. It means that as the bulk is ground into small size (20-50 μm), the surface area of sample can be increased by 27 times, which will notably improve heat transfer. The combined effect with the reduction of internal strain and grain boundaries should be the main reason

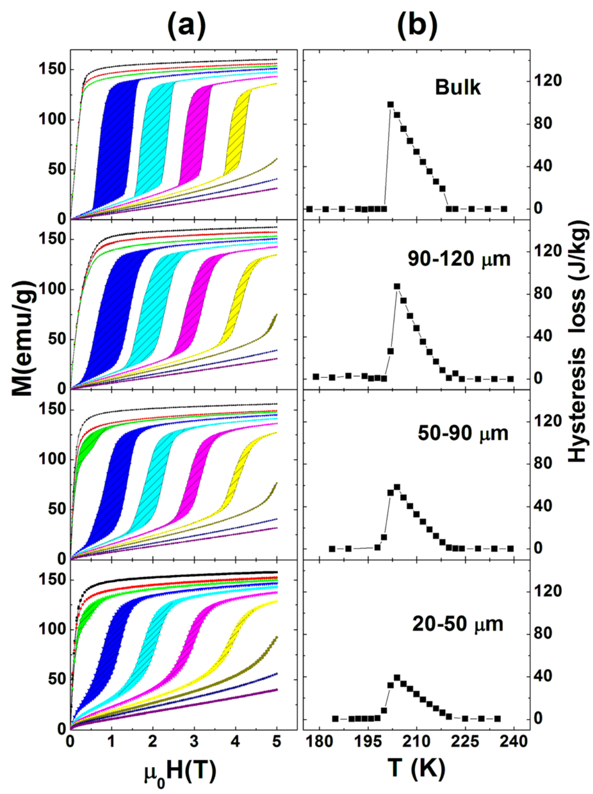

FIG. 1. (Color online) (a) Magnetization isotherms on field increase and decrease for the big (90-120 μm), middle (50-90 μm), and small (20-50 μm) particles, compared to the bulk and (b) the deduced hysteresis loss (enclosed area in a field cycle) as a function of temperature for the corresponding samples.

for the observed reduction of hysteresis in the present systems.

We calculated entropy change ΔS using Maxwell relation. The effective $|\Delta S|$ (not the spike but the high plateau value[11,12]) is 28.8, 27.7, 27.1, and 26.6 J/kgK, and the effective refrigeration capacity RC (after deducting the maximal hysteresis[13]) is 410, 405, 433, and 460 J/kg, for the bulk, big, middle, and small particles under a field change of 0-5 T, respectively. Although $|\Delta S|$ value slightly decreases with reducing particle size, the effective RC increases by a ratio of 12% due to the notable reduction of hysteresis loss. Previous studies suggested that demagnetization effect is considerably large and cannot be neglectable for the irregular powders.[14] Carefully simulating the M-H curves measured at 5 K gives the demagnetization factor of $\sim$0.27 for the present particles ($\geq$20 μm), in good agreement with previous reports.[14] We calculated ΔS from the magnetization after demagnetization correction and found the obtained $|\Delta S|$ enhances little, $\leq$0.5%. Although the magnetization changes much after demagnetization correction, particularly for the low field magnetization, the enclosed area between the two adjacent M-H curves changes little.

Our further studies indicate that the sample cannot be broken up endlessly. When the size is below 10 μm (average $\sim$ 4μm), the sample loses its stability and MCE notably reduces. Fig. 2 displays temperature dependent magnetization (M-T curve) measured under 200 Oe. Upper inset presents M-T curve of the bulk for comparison. One can notice the magnetic transition at $\sim$200 K still remains for the powder, but the magnetization at paramagnetic region becomes high and does not approach zero up to 390 K. One may think about the possible appearance of α-Fe phase. However, careful XRD measurements denied the conjecture (Fig. 3). The XRD peaks become broadening due to fine powder, but no obvious impurity was detected besides 1:13 phase. Left inset of Fig. 3 shows XRD data collected step by step (step: 0.02°) from 43° to 48°. No α-Fe, whose main peak (110) locates at 44.6°, was detected. Right inset is the scanning electron microscope (SEM) photograph of the sample. A rough estimation indicates that the average particle size is about 4 μm. At such particle size, the interactions between particles should be neglectable,[15] and do not affect magnetic properties.

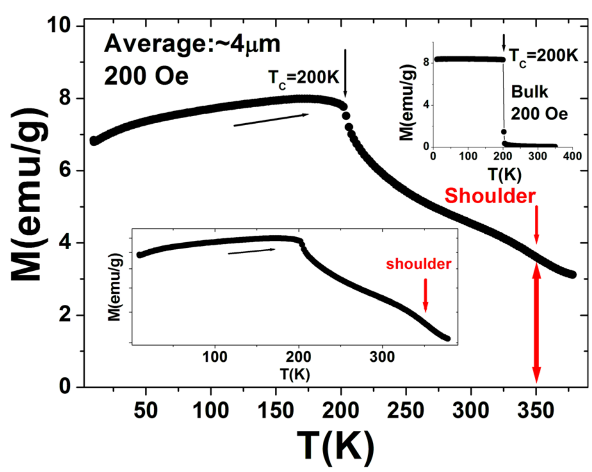

FIG. 2. (Color online) Temperature dependent magnetization (M-T curve) under 200 Oe for the fine powder with size smaller than 10 μm (average $\sim$ 4 μm). Lower inset shows the M-T curve in the semi-log plot. Upper inset presents M-T curve of the bulk for comparison.

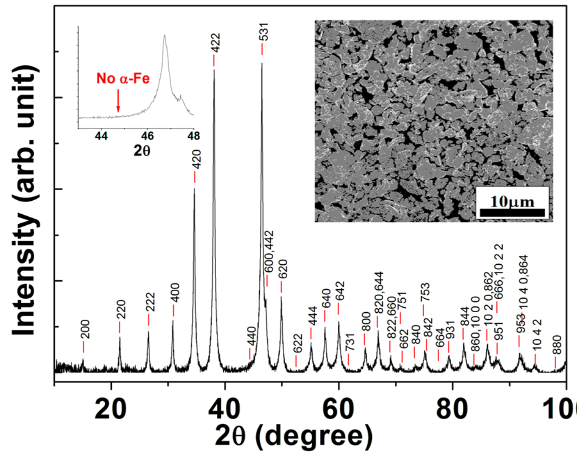

FIG. 3. (Color online) X-ray diffraction data for the fine powder with size smaller than 10 μm (average $\sim$ 4 μm). Left inset shows XRD data collected step by step (step: 0.02°) from 43° to 48°. Right inset is the SEM photograph of the sample.

From Fig. 2, one may notice a shoulder appears around 350 K, which is more distinct in the semi-log plot (see the lower inset of Fig. 2). The high magnetization above 200 K and the obvious shoulder strongly suggest possible appearance of second phase with considerable ratio. However, XRD did not detect any phases besides 1:13 phase. Barcza *et al.*[16] studied the instability of partially hydrogenated La-Fe-Si alloys and found that the sample loses its stability and separates into two 1:13 phases as the sample is only held at its T_C for a period of time. But fully hydrogenated samples do opposite and show good stability. We suppose the shoulder may be the decomposed 1:13 phase. One knows that the interstitial H and C atoms occupy same sites (24d) and play similar roles in the lattice. For the present $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$, C content is not saturated distinctly, which prompts us to think that the observed abnormal thermal magnetization in the fine powder ($<$10 μm, average $\sim$4 μm) might come from the instability of carbides. Such instability might be related to the introduced strain accumulation during grinding process. However, to get the exact reasons, further detailed investigations are still required. Anyway, our investigations reveal the particle size limitation for $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$. As particle size is smaller than 10 μm, the sample may lose stability and cause reduction of MCE.

Figs. 4(a) and 4(b) show magnetization isotherms on field increase and decrease and the calculated entropy change ΔS by Maxwell relation for the fine powder ($<$10 μm, average $\sim$4 μm). The magnetic hysteresis approaches zero at this particle size. The ΔS peak appears around T_C but followed by a long tail with increasing temperature due to the possible existence of second 1:13 phase. Similar to the M-T curve (Fig. 2), a gentle shoulder can be also distinguished around 350 K in the ΔS curves. The maximal $|\Delta S|$ is only 8.0 J/kgK under 5 T, reduced by 3.6 times, and the corresponding RC is 170 J/kg, reduced by more than one half, compared to the bulk.

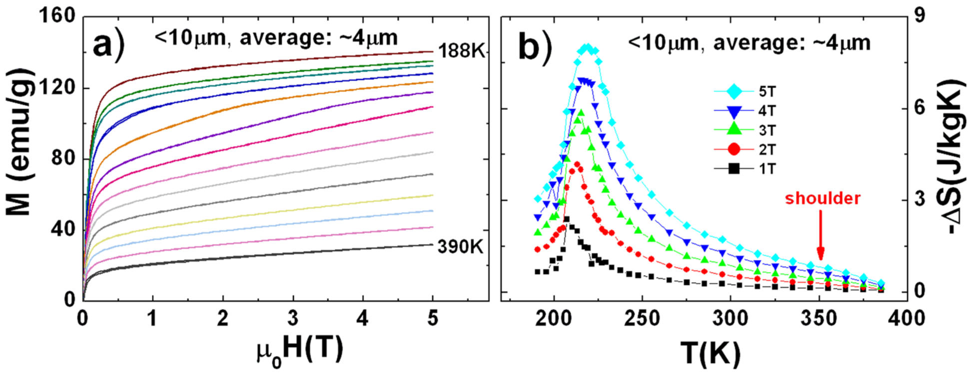

FIG. 4. (Color online) (a) Magnetization isotherms on field increase and decrease and (b) magnetic entropy change as a function of temperature under different magnetic fields for the fine powder with size smaller than 10 μm (average $\sim$ 4 μm).

In summary, particle size dependent hysteresis loss was studied in $La_{0.7}Ce_{0.3}Fe_{11.6}Si_{1.4}C_{0.2}$ first-order systems. Our results indicated that granulating the materials into particles smaller than 120 μm but larger than 20 μm is an effective way to reduce hysteresis loss while maintaining large entropy change and strong RC. Hysteresis loss is getting smaller with reducing the particle size. The maximal hysteresis loss reduces from 98.4 J/Kg at bulk to 38.8 J/Kg at particle size 20-50 μm. The reduced ratio is as high as $\sim$61%. As a result, the effective RC increases by 12% due to the notable reduction of hysteresis loss. The reason can be ascribed to the partially removed internal strain and grain boundaries as well as the notably improved situation of heat transfer caused by the high increase of surface area of sample to volume ratio. More importantly, particle size limitation was observed. The materials cannot be broken up endlessly. When the size is below 10 μm (average $\sim$ 4 μm), the sample may lose its stability and the $|\Delta S|$ notably reduces. These observations provide constructive information on guiding manufacturable process, which will highly benefit practical applications of the MCE materials in refrigeration machines.

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