Particle size dependent hysteresis loss in La$_{0.7}$Ce$_{0.3}$Fe$_{11.6}$Si$_{1.4}$C$_{0.2}$ first-order systems

F. X. Hu, L. Chen, J. Wang, L. F. Bao, J. R. Sun, and B. G. Shen

Beijing National Laboratory for Condensed Matter Physics and State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China

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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 [ΔS] 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 [ΔS] notably reduces.


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$_5$Si$_2$Ge$_2$, MnFe$_{0.45}$As$_{0.55}$, LaFe$_{13}$, has attracted much attention due to easy preparation, cheap raw materials, and non-toxic characters. Several demonstrators using La(Fe,Si)$_{13}$-based compounds as working substances have been tested and confirmed the excellent performance of the compounds. 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$_5$Si$_2$Ge$_2$ by measuring magnetic relaxation, and the results were interpreted in terms of a thermal activation model. 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.

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. studied Gd$_5$Ge$_4$ 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. 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.

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$_2$ 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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4) Author to whom correspondence should be addressed. Electronic mail: fxhu@iphy.ac.cn.
~4 μm), samples lose their stability and the MCE remarkably reduces.

We prepared La0.7Ce0.3Fe11.6Si1.4C0.2 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 NaZn13-type structure. Powder x-ray diffraction using Cu Kα radiation indicated that the phase is clean for the C-doped samples.

The polycrystalline bulk La0.7Ce0.3Fe11.6Si1.4C0.2 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 (~4 μm in average). Meanwhile, an irregular single fragment (mass: 2.7 mg, size <1×1×1 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 TC and saturated magnetization remain unchanged as the particle size is above 20 μm. Thermal magnetization measurements under 0.02 T indicated that the TC, for the big (90-120 μm), middle (50-90 μm), and small (20-50 μm) particles, fixes at the same position. ~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 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.

![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.](image-url)
for the observed reduction of hysteresis in the present systems.

We calculated entropy change $\Delta S$ 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 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 $10\ \mu m$ (average $\sim 4\ \mu m$), 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 $\alpha$-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: $0.02^\circ$) from $43^\circ$ to $48^\circ$. No $\alpha$-Fe, whose main peak (110) locates at $44.6^\circ$, 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 $4\ \mu m$. At such particle size, the interactions between particles should be neglectable,$^{15}$ and do not affect magnetic properties.

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. Barca 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 $\text{La}_{0.7}\text{Ce}_{0.3}\text{Fe}_{11.6}\text{Si}_{1.4}\text{C}_{0.2}$, C content is not saturated distinctly, which prompts us to think that the observed abnormal thermal magnetization in the fine powder ($<10\ \mu m$, average $\sim 4\ \mu m$) 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 $\text{La}_{0.7}\text{Ce}_{0.3}\text{Fe}_{11.6}\text{Si}_{1.4}\text{C}_{0.2}$. As particle size is smaller than $10\ \mu m$, 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 $\Delta S$ by Maxwell relation for the fine powder ($<10\ \mu m$, average $\sim 4\ \mu m$). The magnetic hysteresis approaches zero at this particle size. The $\Delta S$ 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 $\Delta S$ 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. 2. (Color online) Temperature dependent magnetization (M-T curve) under 200 Oe for the fine powder with size smaller than $10\ \mu m$ (average $\sim 4\ \mu m$). Lower inset shows the M-T curve in the semi-log plot. Upper inset presents M-T curve of the bulk for comparison.
In summary, particle size dependent hysteresis loss was studied in La$_{0.7}$Ce$_{0.3}$Fe$_{11.6}$Si$_{1.4}$Co$_{0.2}$ first-order systems. Our results indicated that granulating the materials into particles smaller than 120 $\mu$m but larger than 20 $\mu$m 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 $\mu$m. The reduced ratio is as high as 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 $\mu$m (average $\sim$ 4 $\mu$m), 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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