Vol 18 No 10, October 2009
1674-1056/2009/18(10)/4366–04

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

High-resolution transmission electron microscopy and bulk magnetometry study of $LaFe_{11.5}Si_{1.5}$ compound*

Zou Jun-Ding(邹君鼎)[a)†], Li Wei(李 卫)[a)], and Shen Bao-Gen(沈保根)[b)]

[a)] *Division of Functional Materials, Central Iron and Steel Research Institute, Beijing* 100081, *China*

[b)] *State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

(Received 5 November 2008; revised manuscript received 17 March 2009)

This paper studies the microstructural and magnetic properties of $LaFe_{11.5}Si_{1.5}$ compound by means of high-resolution transmission electron microscope and bulk magnetometry measurements. The crystalline structure is accompanied with the noncrystalline and nanocrystalline structures. This characteristic is the reflection of the crystalline process held by quenching. The inverse susceptibilities diverge and deviate from Curie–Weiss law under low applied magnetic fields. This paper proposes the possible mechanism between the anomalous susceptibilities and microstructure, and offers a perspective on the magnetic properties of metastable intermetallic compounds.

Keywords: high-resolution transmission electron micropscope, magnetic susceptibility
PACC: 6114R, 7540C

1. Introduction

Recently, it has been demonstrated that $NaZn_{13}$-type $LaFe_{13-x}Si_x$ compounds exhibit large magnetocaloric effec (MCE),[1−5] large spontaneous magnetovolume effect,[1,2,6−9] and itinerant electron metamagnetism (IEM),[6−10] etc., near first-order phase transition. Due to the large MCE, $LaFe_{13-x}Si_x$ compounds are widely investigated for their potential applications as favorable magnetic refrigerants. The long-term heat treatment and quenching are often used to obtain single phase samples. In fact, the quenched $LaFe_{13-x}Si_x$ compounds are at metastable state. For the heat-treated samples, the compositions are homogeneous but the sizes of grains are inhomogeneous. These characteristics are very important for entirely understanding $LaFe_{13-x}Si_x$ compounds, and have notable influence on the magnetic properties during the practical application. Therefore, it would be interesting to explore the influence of microscopic crystalline process on the macroscopic properties. Here, high-resolution transmission electron microscope (HRTEM) is used to study the unique crystalline process of $LaFe_{13-x}Si_x$ frozen by liquid nitrogen quenching. The influence of the crystalline process on the magnetic properties will be uncovered by the bulk magnetometry study.

2. Experimental details

The $LaFe_{11.5}Si_{1.5}$ sample was prepared by arc melting the pure metals under ultra-pure argon gas in a water-cooled copper crucible. The purity of the raw materials is 99.9% for lanthanum and iron, and 99.99% for silicon. The subsequent heat treatment was carried out in a high vacuum quartz tube at 1343 K for 58 days. Subsequently, the sample was quenched in liquid nitrogen. The $NaZn_{13}$-type structure is confirmed by the x-ray powder diffraction study. The HRTEM analysis with conventional powder samples was carried out on a JEM 2010 TEM with a 200-kV accelerating voltage. Magnetization measurements were carried out by using physical properties measurement system (PPMS) from Quantum Design Inc with zero-field-cooling and fixed point model in fields up to 5 T.

3. Results and discussion

The TEM image and a selected area diffraction (SAD) pattern along [111] zone-axes of $LaFe_{11.5}Si_{1.5}$ are shown in Figs.1(a) and 1(b), respectively. The superimposed rings of SAD identified the existence of nanocrystal.[11] Two HRTEM images along [111] zone-axes, shown in Figs.2(a) and 2(b), reveal that the noncrystalline structure exists both in crystal fringe

*Project supported by the National Natural Science Foundation of China (Grant No 50801015), the National High Technology Research and Development Program of China (Grant No 2007AA03Z458).

†Corresponding author. E-mail: zjd@g203.iphy.ac.cn

and interior. The black arrow in Fig.2(a) demonstrates the amorphous structure, and the black arrow in Fig.2(b) indicates the crystalline structure surrounded by amorphous structure. The insets show the corresponding fast Fourier transformations (FFT). The diffraction spots relate to the single crystal, and diffraction halo relate to amorphous structure. Following the boundary between the amorphous and crystalline structure in Fig.2(a), the crystalline intergradations can be observed. Figure 2(b) represents the crystalline structure forming and enlarging. The HRTEM images reveal the crystalline process of quenched $LaFe_{11.5}Si_{1.5}$ sample.

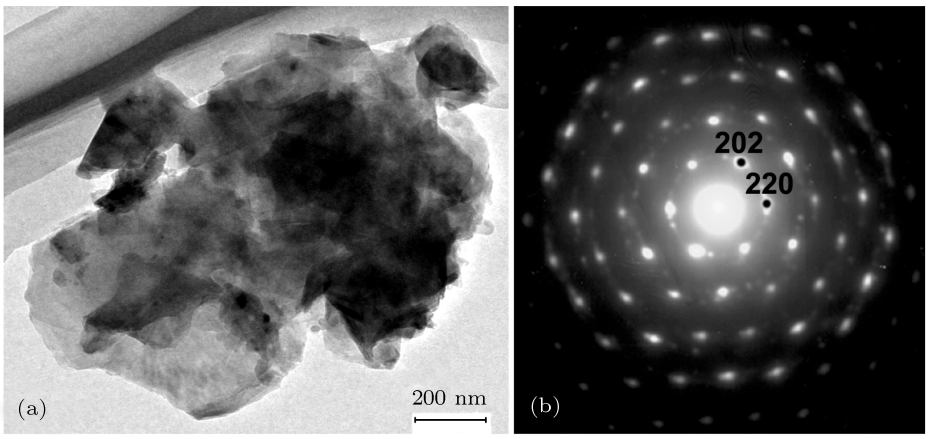


Fig.1. (a) Room temperature TEM image. (b) The corresponding SAD pattern along [111] zone-axes.

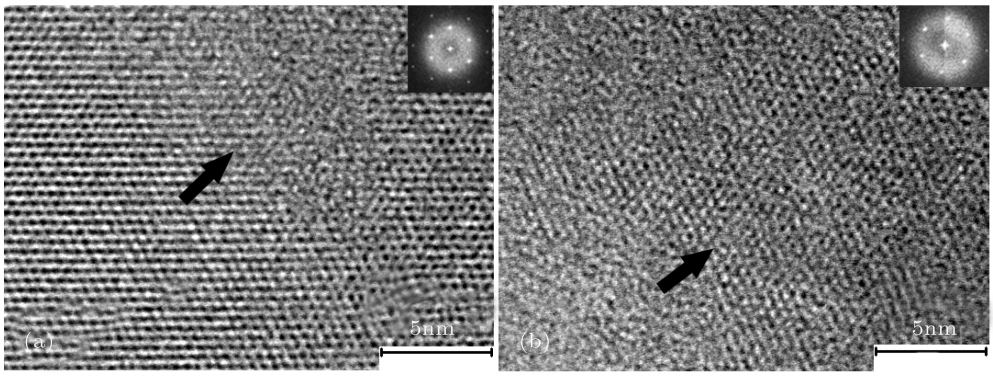


Fig.2. (a) and (b) HRTEM images along [111] zone-axes. The black arrow in (a) demonstrates the noncrystalline structure, and the black arrow in (b) indicates the crystalline structure surrounded by amorphous area.

The origin of noncrystalline structure is needed for a thorough study. Rapid solidification from the melt is usually used to produce amorphous alloys.[12] Indeed, the poor combination capacity between La and Fe in $LaFe_{13-x}Si_x$ compounds is the key reason for the appearance of noncrystalline structures. The crystalline processes of $LaFe_{13-x}Si_x$ compounds are very slow even in the case undergoing long-term heat treatment at high temperature. This leads the $LaFe_{13-x}Si_x$ compounds to be metastable. It is inevitable that some crystalline processes cannot be entirely finished. The origin of nanocrystal is similar with that of noncrystal. The quenched $LaFe_{13-x}Si_x$ compounds are very fragile, mainly due to the inhomogeneity in the sizes of crystalline grains and the imperfection of the crystalline process.

Figures 3(a) and 3(b) show the temperature dependences of magnetizations. The sample presents typical characteristic of first-order phase transition, demonstrated by the high temperature shift of T_C with applied

field (from 191 K at 20 mT to 211 K at 5 T). Figures 3(c) and 3(d) show the temperature-dependent inverse susceptibilities under different applied fields. The curves of χ^{-1}–T under weak applied field are inconsistent above $T_{\rm C}$ and deviating from Curie–Weiss law, but good consistencies are observed under strong applied field. These behaviors go against the usual expectation that the inverse susceptibilities above $T_{\rm C}$ are coincident.

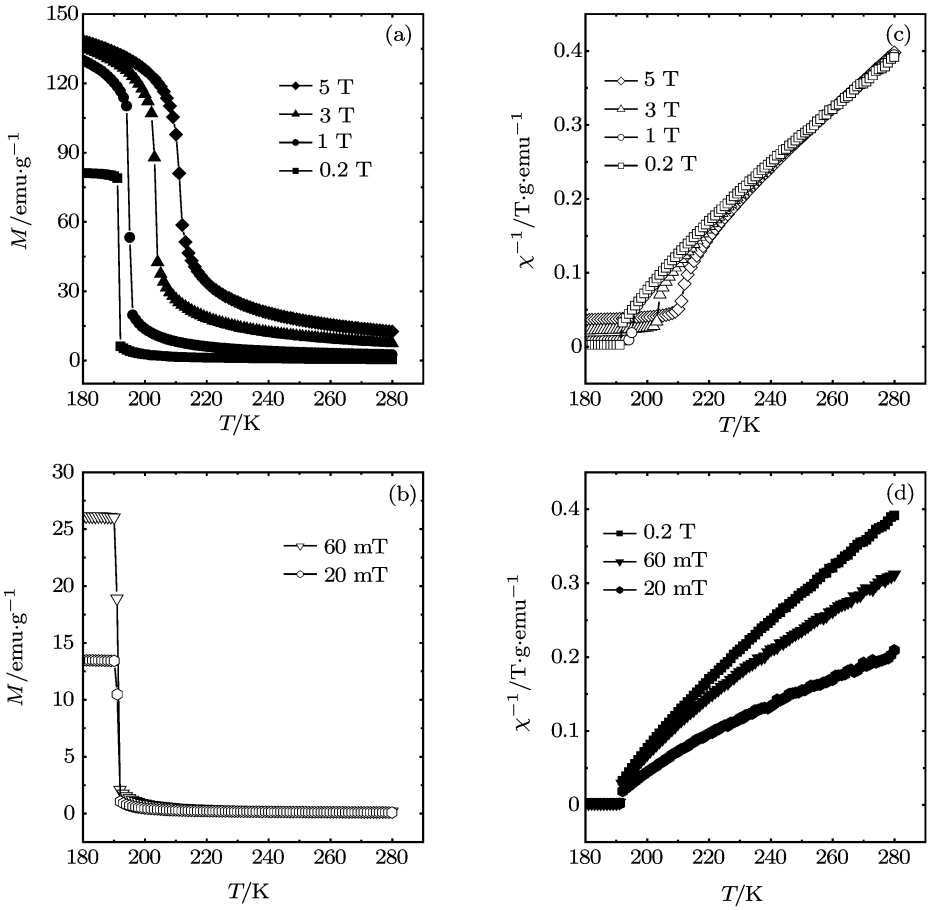


Fig.3. (a) and (b) temperature dependences of magnetizations. (c) and (d) inverse susceptibilities measured on temperature increasing under different applied field after zero-field cooling. Solid lines are guides for the eye.

We speculate that the key reasons for anomalous susceptibilities are the noncrystalline and nanocrystalline structures. The obvious differences in the magnetic properties between amorphous and crystalline states are still elusive, either in experimental or theoretical representations. In a sense, the amorphous state is similar to the state of melting. Moreover, $LaFe_{13-x}Si_x$ compounds show itinerant electron ferromagnetism and may be easily subjected to the disorder of atoms or the finite-size of the grains. The results of this paper will help to understand the magnetic behaviors of amorphous structure. According to the superimposed rings on the SAD image, we can identify the existence of nanocrystal. Usually, the total angular momentum increases, and the Curie temperature decreases if the size of the grains decreases continuously.[13–15] Therefore, the χ^{-1}–T relations will deviate downward from the Curie–Weiss law when both microcrystalline and nanocrystalline structures exist.

4. Conclusion

$LaFe_{13-x}Si_x$ compounds are looked at as attractive candidate materials for magnetic refrigeration. The microstructural information is important for the MCE research and practical application in magnetic refrigeration, but none of these kinds of research have been carried out. Here we observe that the crystalline structure is accompanied with the noncrystalline and nanocrystalline structures which may originate from the intrinsic

difficulty in the combining capacity and the slow crystalline processes. The amorphous and nanocrystalline structure may lead the inverse susceptibilities above T_C to deviate from each other and depart dramatically from Curie–Weiss law under low applied field. The χ^{-1}–T slopes of noncrystalline and nanocrystalline structures are smaller than that of crystalline structure due partly to the increase in the magnetic moment. The inverse susceptibilities above T_C show good a consistence under strong applied field because the signals of minority amorphous and nanocrystalline structure are overwhelmed by that of majority crystalline structure. Further effort should be made to fully understand the magnetic behaviors of $LaFe_{13-x}Si_x$ compounds.

References

[1] Hu F X, Shen B G, Sun J R, Cheng Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675

[2] Hu F X, Shen B G, Sun J R, Wang G J and Cheng Z H 2002 *Appl. Phys. Lett.* **80** 826

[3] Fujita A, Fujieda S, Hasegawa Y and Fukamichi K 2003 *Phys. Rev.* B **67** 104416

[4] Zou J D, Shen B G and Sun J R 2007 *J. Phys.: Condens. Matter* **19** 196220

[5] Zou J D, Shen B G, Gao B, Shen J and Sun J R 2009 *Adv. Mater.* **21** 693

[6] Fujita A, Akamatsu Y and Fukamichi K 1999 *J. Appl. Phys.* **85** 4756

[7] Fujita A, Fujieda S, Fukamichi K, Mitamura H and Goto T 2001 *Phys. Rev.* B **65** 014410

[8] Fujita A, Fukamichi K, Yamada M and Goto T 2003 *J. Appl. Phys.* **93** 7263

[9] Fujita A, Fukamichi K, Wang J T and Kawazoe Y 2003 *Phys. Rev.* B **68** 104431

[10] Fujieda S, Fujita A, Fukamichi K, Yamazaki Y and Lijima Y 2001 *Appl. Phys. Lett.* **79** 653

[11] de Graef M 2003 *Introduction to Conventional Transmission Electron Microscopy* (Cambridge: Cambridge University Press)

[12] O'Handley R C 2000 *Modern Magnetic Materials: Principles and Applications* (New York: John Wiley & Sons, Inc)

[13] Hendriksen P V, Linderoth S and Lindgard P A 1993 *Phys. Rev.* B **48** 7259

[14] Billas I M L, Becker J A, Chatelain A and de Heer W A 1993 *Phys. Rev. Lett.* **71** 4067

[15] Billas I M L, Chatelain A and de Heer W A 1994 *Science* **265** 1682