AIP | Journal of Applied Physics

Mechanical properties and magnetocaloric effects in La(Fe, Si)13 hydrides bonded with different epoxy resins

Hu Zhang, YuJie Sun, YaWei Li, YuanYuan Wu, Yi Long, Jun Shen, FengXia Hu, JiRong Sun, and BaoGen Shen

Citation: Journal of Applied Physics **117**, 063902 (2015); doi: 10.1063/1.4908018
View online: http://dx.doi.org/10.1063/1.4908018
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/6?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **117**, 063902 (2015)

Mechanical properties and magnetocaloric effects in La(Fe, Si)$_{13}$ hydrides bonded with different epoxy resins

Hu Zhang,[1,a)] YuJie Sun,[1] YaWei Li,[1] YuanYuan Wu,[1] Yi Long,[1] Jun Shen,[2] FengXia Hu,[3] JiRong Sun,[3] and BaoGen Shen[3]
[1]*School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, People's Republic of China*
[2]*Key laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[3]*State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

(Received 25 November 2014; accepted 2 February 2015; published online 11 February 2015)

The mechanical properties and magnetocaloric effect (MCE) of bonded La(Fe, Si)$_{13}$ hydrides have been studied in detail. The mechanical strength increases with increasing the grade of epoxy resin from E-20 to E-51. This occurs because more pores and boundaries are filled with high grade resin since high epoxide content increases the degree of crosslinking and reduces the viscosity and shrinkage of resin. The compressive strength reaches 162 MPa for the bonded LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$H$_{1.8}$ with 3 wt. % E-51, which is 35% higher than that of bulk LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$ compound (120 MPa). The mass ΔS_M values remain almost same in bonded hydrides and are in a good agreement with the theoretical value. The maximum volumetric ΔS_M values are 61.8, 58.0, and 54.7 mJ/cm^3 K for bonded hydrides with epoxy resins E-20, E-44, and E-51, respectively, much higher than those of some magnetocaloric materials in same temperature range. The improved mechanical properties and large MCE indicate that bonded LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$H$_{1.8}$ is a promising material for room temperature magnetic refrigeration. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4908018]

I. INTRODUCTION

Recently, magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted considerable research attention due to its various advantages in comparison with conventional gas compression-expansion technique, such as energy efficiency and environment safety.[1–4] Magnetocaloric materials are the core part of magnetic refrigeration technology, and therefore, many advanced magnetic materials with large MCE especially near room temperature have been explored and reported so far.[5–11] In these materials, La(Fe, Si)$_{13}$-based compounds with NaZn$_{13}$-type (1:13) structure, exhibiting itinerant electron metamagnetic (IEM) transition, have been considered among the most promising materials for room temperature magnetic refrigeration.[12–14] However, the Curie temperature (T_C) of La(Fe, Si)$_{13}$ compound is usually lower than 210 K, which hinders the practical applications of La(Fe, Si)$_{13}$-based material around room temperature.[12,15] It has been proved that the introduction of interstitial H atoms could lead to lattice expansion and enhance T_C significantly up to around 350 K. Besides, the MCE of hydride remains high while the magnetic hysteresis can be very small.[16,17]

Although La(Fe, Si)$_{13}$ hydride exhibits excellent MCE around room temperature, the intrinsic brittleness of 1:13 phase and hydrogen cracking during the hydrogenation process make the hydride only exist in powder form, which does not meet the shape requirements for magnetic refrigerants used in magnetic refrigeration applications.[18] Lyubina *et al.* pressed the La(Fe, Si)$_{13}$ powder into porous structure by hot-pressing technique, and found that the porous La(Fe, Si)$_{13}$ material exhibits much better mechanical properties and lower hysteresis than those of bulk compound.[19] However, hot-pressing technique may not be suitable for the processing of La(Fe, Si)$_{13}$ hydride due to the instability of hydride when temperature is higher than 150 °C.[20] Very recently, we mixed La(Fe, Si)$_{13}$ hydride powder with epoxy resin and successfully produced bonded La(Fe, Si)$_{13}$ hydride by cold-pressing technique; such material exhibits better mechanical properties than those of transitional bulk compound.[21] Moreover, Skokov *et al*. found that the adiabatic temperature change (ΔT_{ad}) of polymer-bonded La(Fe, Si)$_{13}$ is 10% higher than that in the initial bulk material, further indicating that bonded La(Fe, Si)$_{13}$ material could be desirable candidate for magnetic refrigeration around room temperature.[22] In present work, we further studied the mechanical properties and MCE in bonded La(Fe, Si)$_{13}$ hydrides with different epoxy resins.

II. EXPERIMENTAL DETAILS

The detail of sample preparation for LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$ and LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$H$_{1.8}$ has been described elsewhere.[23,24] LaFe$_{11.7}$Si$_{1.3}$C$_{0.2}$H$_{1.8}$ powders (particle size $<$ 0.1 mm) were mixed with 3 wt. % combination of epoxy resin and Mannich amide T-31, in which different commercial epoxy resins E-20, E-44, and E-51 were used, respectively. The mixed powders were pressed into cylindrical pieces of $\Phi 10 \times 10$ mm under a pressure of 900 MPa and then solidified at room temperature for 5 days. For comparison, an unbound hydride

---

[a)] Author to whom correspondence should be addressed. Electronic mail: zhanghu@ustb.edu.cn. Tel.: +86-10-62333514.

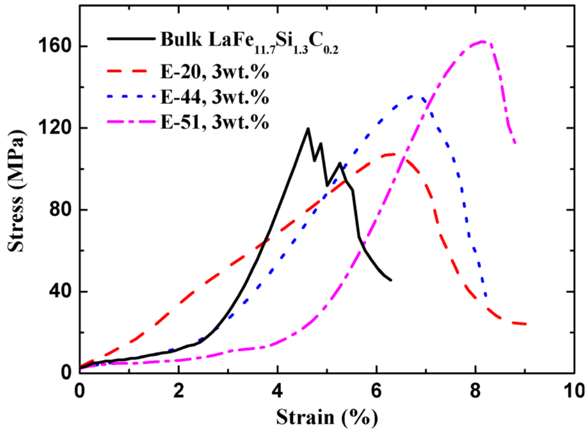

FIG. 1. Compressive stress-strain curves for bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with different epoxy resins in comparison with bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound.

sample was also obtained by pressing the pure $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ powder into a cylinder. The density of the samples was examined by Archimedes method. Microstructure was investigated by scanning electron microscopy (SEM) using a LEO-1450 microscope. Compression test was performed using a universal material testing machine with a loading rate of 9 μm/s under ambient temperature. Magnetic measurement was performed by employing a VersaLab VSM (Vibrating Sample Magnetometer) system from Quantum Design, Inc.

III. RESUTLS AND DISCUSSION

Figure 1 shows the compressive stress-strain curves for bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with different epoxy resins. It has to be pointed out that the unbound hydride sample is not structurally stable for the compression test, so the bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound was machined into a cylinder of $\Phi10\times10$ mm and tested for comparison. The stress-strain curve of bulk sample presents a short yield stage and then drops quickly without further plastic deformation, indicating the intrinsic brittleness of bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound. All bonded hydrides exhibit larger maximum strain than that of bulk sample. This is attributed to the porous architecture of bonded materials, which shows a large strain due to the densification under stress. In addition, it is found that the compressive strength of bonded hydride increases with grade of epoxy resin. The compressive strength reaches 162 MPa for the bonded material with E-51, 35% higher than that of bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound (120 MPa).[21] This result indicates that the bonded hydride with E-51 is mechanically stronger than both the unbound hydride sample and the bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound before hydrogenation.

In order to further understand the improvement of mechanical stability in bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$, the SEM investigation was carried out and the images of bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound and bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with epoxy resins E-20 and E-51 are shown for comparison in Fig. 2. When compared with the bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound, the bonded hydrides exhibit porous architecture, leading to the large maximum strain. Moreover, the porous architecture could also reduce the magnetic hysteresis loss by partially removing the internal strain and grain boundaries, which is favorable to the applications of magnetic refrigeration. The epoxy resin fills in the pores and boundaries between different particles as gray area. There are more unfilled pores and boundaries (black area) in bonded material with E-20 than in the one with E-51. It is known that the epoxide content increases with the increase in epoxy resin grade, which would enhance the degree of crosslinking and reduce the viscosity and shrinkage of resin. Therefore, more pores and boundaries are filled by epoxy resin E-51 with high degree of crosslinking and low viscosity and shrinkage, which improves the mechanical properties by enhancing the binding force between different particles. It is also noted that there are still some unfilled pores and boundaries in the bonded hydride with E-51, suggesting that the mechanical properties may be further improved by increasing the resin content.

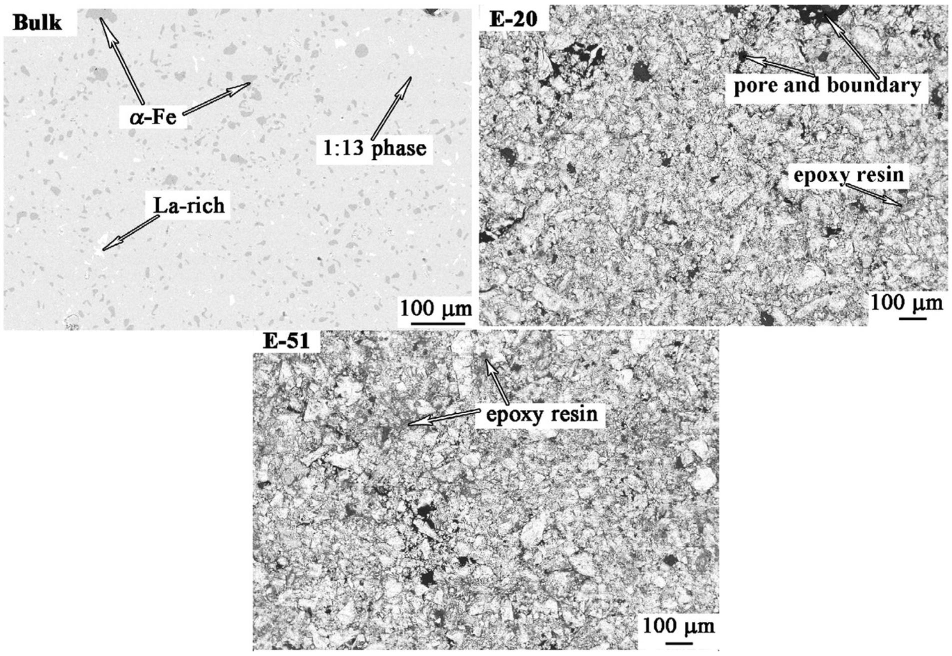

FIG. 2. SEM images of bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ compound and bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with epoxy resins E-20 and E-51, respectively.

Figure 3 shows the magnetization isotherms of the unbound $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ and of the sample bonded with epoxy resin E-51, respectively. It is known that $LaFe_{11.7}Si_{1.3}$ compound exhibits considerable magnetic hysteresis loss of 41 J/kg, which reduces the effective refrigerant capacity.[23] Here, the *M-H* curves around the transition temperature were measured in field increasing and decreasing modes in order to investigate the magnetic reversibility. No magnetic hysteresis is observed in the magnetization isotherms for unbound hydride. The elimination of magnetic hysteresis may occur due to (1) the significant reduction of internal strain and grain boundaries in hydride powders[19,25] and (2) the weakening of first-order magnetic transition caused by introduction of C and H.[23,26] Moreover, the introduction of non-magnetic resin is not affecting the reversibility of field-dependent magnetic transformation, which is beneficial to the practical applications of magnetic refrigeration. Figure 4 shows the Arrott plots of all materials just above the T_C (i.e., $T = 332$ K). Unlike the La(Fe, Si)$_{13}$ materials with strong first-order phase transition which normally exhibit clear negative slope of Arrott plots, here all the curves exhibit an inflection point, proving the weak first-order nature of the magnetic transition in these hydrides.[17]

Figure 5(a) shows the temperature dependence of magnetic entropy change ΔS_M for bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with different epoxy resins in comparison with unbound one under the magnetic field change of 2 T. The maximum ΔS_M values around $T_C = 325$ K are 11.0, 10.8, 10.7, and 10.5 J/kg K for unbound $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ and bonded hydrides with epoxy resins E-20, E-44, and E-51, respectively. The ΔS_M values of bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ are only a little lower than that of unbound material. Considering that the epoxy resin will not contribute to MCE, the theoretical ΔS_M value of bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with 3 wt.% resin is calculated to be 10.67 J/kg K. Therefore, the experimental ΔS_M values of bonded hydrides are in a good agreement with the theoretical value.

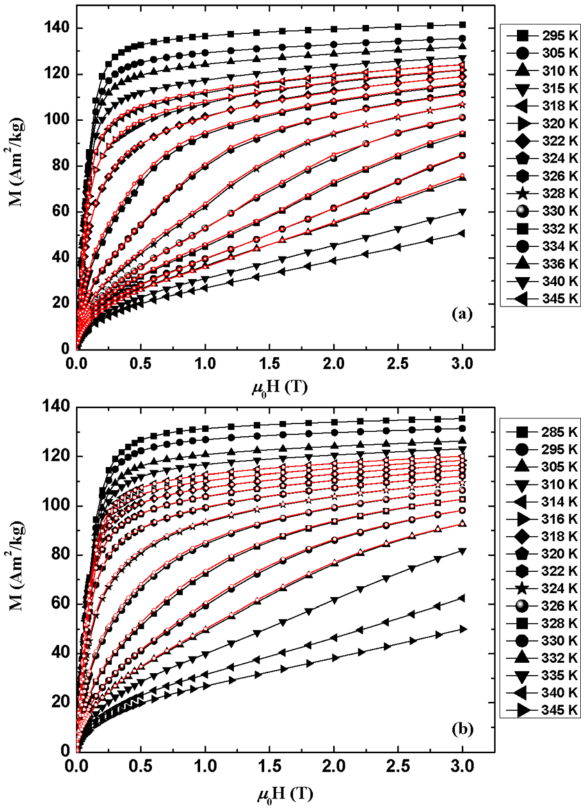

FIG. 3. Magnetization isotherms of unbound $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ and bonded one with epoxy resin E-51, respectively.

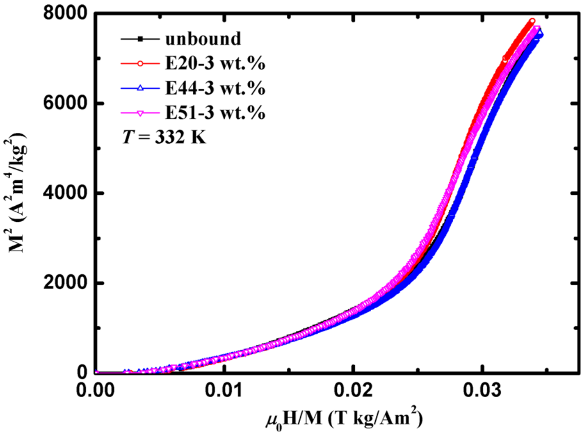

FIG. 4. Arrott plots of all materials just above the T_C.

Gschneidner *et al.* pointed out that the engineer or designer of magnetic refrigerator needs to know the cooling per unit volume, so presenting the ΔS_M using the volumetric unit of mJ/cm^3 K is more practical than using J/kg K.[2] Based on that, the density was examined for all materials shown in

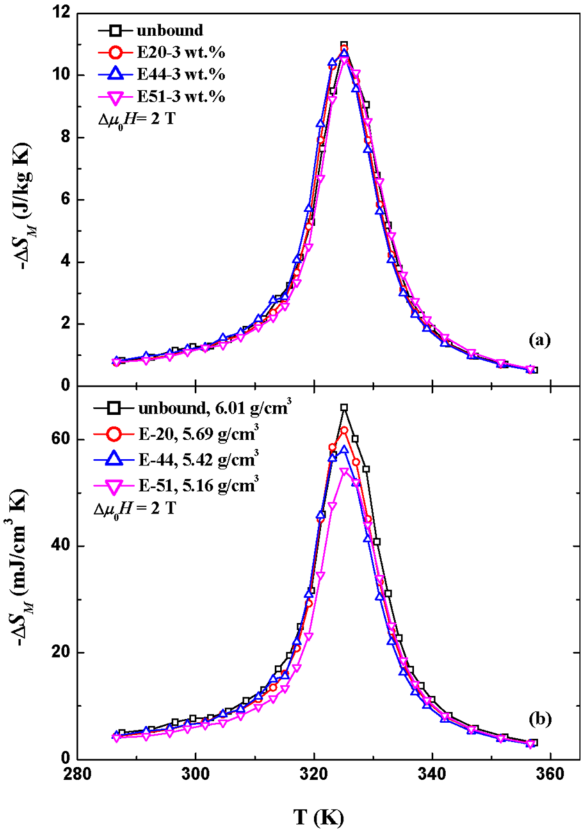

FIG. 5. Temperature dependences of mass (a) and volumetric (b) ΔS_M for bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ with different epoxy resins in comparison with unbound one for a field change of 2 T.

Fig. 5(b) and then the ΔS_M was presented using mJ/cm^3 K units as shown in Fig. 5(b). The maximum volumetric ΔS_M values are 66.0, 61.8, 58.0, and 54.7 mJ/cm^3 K for unbound $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ and bonded hydrides with epoxy resins E-20, E-44, and E-51, respectively. The reduction of volumetric ΔS_M between unbound and bonded hydrides is mainly due to the introduction of non-magnetic epoxy resins in the bonded materials. In addition, it is seen that the volumetric ΔS_M decreases in bonded hydrides with the increase in epoxy resin grade. This is because the density of bonded materials becomes lower with high grade resin, which results in the lower volumetric ΔS_M even though the mass ΔS_M values are nearly same. However, it should be pointed out that the volumetric ΔS_M values for all bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ hydrides are still much higher than those of some other magnetocaloric materials in same temperature range, such as Nd_2Fe_{17} (25 mJ/cm^3 K at 325 K)[27] and Gd_7Pd_3 (22 mJ/cm^3 K at 323 K).[28] In addition to the MCE and mechanical properties, thermal conductivity is considered as another important property of magnetocaloric material which quantifies the efficiency of heat transfer from the material to surrounding environment. Unfortunately, relevant research on thermal conductivity is very few so far. Very recently, Pulko *et al.* reported that the thermal conductivity of epoxy-bonded La-Fe-Co-Si plates can be improved by increasing the content of La-Fe-Co-Si particles,[29] which is similar to the result of the study of porous La-Fe-Si/Cu composite.[30] Considering the lower thermal conductivity of epoxy resin in comparison with that of $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ particles, we speculate that the thermal conductivity is expected to be lowered by introducing resin in the bonded hydrides. However, more work needs to be conducted in order to (1) confirm this speculation and (2) improve the thermal conductivity of bonded hydrides.

IV. CONCLUSIONS

In conclusion, the mechanical properties are significantly improved in bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ hydrides in comparison with those of unbound hydride and bulk $LaFe_{11.7}Si_{1.3}C_{0.2}$ material. In addition, more pores and boundaries could be filled with increasing the grade of epoxy resin due to the enhancement of crosslinking degree and the reduction of resin viscosity and shrinkage, which would then improve the mechanical properties by enhancing the binding force between different particles. The mass ΔS_M values remain nearly unchanged in bonded hydrides and are in a good agreement with the theoretical value of 10.67 J/kg K. The maximum volumetric ΔS_M values are 66.0, 61.8, 58.0, and 54.7 mJ/cm^3 K for unbound $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ and bonded hydrides with epoxy resins E-20, E-44, and E-51, respectively, which are much higher than those of some materials in same temperature range. The enhanced mechanical properties and large MCE without hysteresis loss suggest that bonded $LaFe_{11.7}Si_{1.3}C_{0.2}H_{1.8}$ is a good candidate of room temperature magnetic refrigeration materials.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51371026 and 11274357), the Hi-Tech Research and Development program of China (2011AA03A404), and the Fundamental Research Funds for the Central Universities (FRF-TP-14-011A2).

[1] C. B. Zimm, A. Jastrab, A. Sternberg, V. K. Pecharsky, K. A. Gschneidner, Jr., M. Osborne, and I. Anderson, Adv. Cryog. Eng. **43**, 1759 (1998).
[2] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[3] A. M. Tishin and Y. I. Spichkin, in *The Magnetocaloric Effect and its Applications*, edited by J. M. D. Coey, D. R. Tilley, and D. R. Vij (IOP Publishing, Bristol, 2003).
[4] O. Gutfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, Adv. Mater. **23**, 821 (2011).
[5] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[6] F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[7] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, Phys. Rev. B **65**, 014410 (2001).
[8] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[9] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).
[10] T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, Nature Mater. **4**, 450 (2005).
[11] F. X. Hu, B. G. Shen, and J. R. Sun, Appl. Phys. Lett. **76**, 3460 (2000).
[12] B. G. Shen, J. R. Sun, F. X. Hu, H. W. Zhang, and Z. H. Cheng, Adv. Mater. **21**, 4545 (2009).
[13] J. Liu, M. Krautz, K. Skokov, T. G. Woodcock, and O. Gutfleisch, Acta Mater. **59**, 3602 (2011).
[14] H. Zhang, F. X. Hu, J. R. Sun, and B. G. Shen, Sci. China Phys. Mech. **56**, 2302 (2013).
[15] S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[16] A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[17] Y. F. Chen, F. Wang, B. G. Shen, F. X. Hu, J. R. Sun, G. J. Wang, and Z. H. Cheng, J. Phys.: Condens. Matter **15**, L161 (2003).
[18] J. D. Moore, D. Klemm, D. Lindackers, S. Grasemann, R. Träger, J. Eckert, L. Löber, S. Scudino, M. Katter, A. Barcza, K. P. Skokov, and O. Gutfleisch, J. Appl. Phys. **114**, 043907 (2013).
[19] J. Lyubina, R. Schäfer, N. Martin, L. Schultz, and O. Gutfleisch, Adv. Mater. **22**, 3735 (2010).
[20] Y. F. Chen, F. Wang, B. G. Shen, G. J. Wang, and J. R. Sun, J. Appl. Phys. **93**, 1323 (2003).
[21] H. Zhang, Y. J. Sun, E. Niu, F. X. Hu, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **104**, 062407 (2014).
[22] K. P. Skokov, D. Y. Karpenkov, M. D. Kuz'min, I. A. Radulov, T. Gottschall, B. Kaeswurm, M. Fries, and O. Gutfleisch, J. Appl. Phys. **115**, 17A941 (2014).
[23] H. Zhang, B. G. Shen, Z. Y. Xu, X. Q. Zheng, J. Shen, F. X. Hu, J. R. Sun, and Y. Long, J. Appl. Phys. **111**, 07A909 (2012).
[24] H. Zhang, Y. Long, E. Niu, X. P. Shao, J. Shen, F. X. Hu, J. R. Sun, and B. G. Shen, J. Appl. Phys. **113**, 17A911 (2013).
[25] F. X. Hu, L. Chen, J. Wang, L. F. Bao, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **100**, 072403 (2012).
[26] J. Shen, B. Gao, H. W. Zhang, F. X. Hu, Y. X. Li, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **91**, 142504 (2007).
[27] S. Y. Dan'kov, V. V. Ivtchenko, A. M. Tishin, K. A. Gschneidner, Jr., and V. K. Pecharsky, Adv. Cryog. Eng. **46**, 397 (2000).
[28] F. Canepa, M. Napoletano, and S. Cirafici, Intermetallics **10**, 731 (2002).
[29] B. Pulko, J. Tusek, J. D. Moore, B. Weise, K. Skokov, O. Mityashkin, A. Kitanovski, C. Favero, P. Fajfar, O. Gutfleisch, A. Waske, and A. Poredos, J. Magn. Magn. Mater. **375**, 65 (2015).
[30] J. Lyubina, U. Hannemann, L. F. Cohen, and M. P. Ryan, Adv. Energy Mater. **2**, 1323 (2012).