Magnetic phase transition and magnetocaloric effect in Dy12Co7 compound

Q. Y. Dong, J. Chen, X. Q. Zhang, X. Q. Zheng, J. R. Sun et al.

Citation: J. Appl. Phys. **114**, 173911 (2013); doi: 10.1063/1.4829281
View online: http://dx.doi.org/10.1063/1.4829281
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v114/i17
Published by the AIP Publishing LLC.

Magnetic phase transition and magnetocaloric effect in $Dy_{12}Co_7$ compound

Q. Y. Dong,[1,a)] J. Chen,[2,3] X. Q. Zhang,[2] X. Q. Zheng,[2] J. R. Sun,[2] and B. G. Shen[2]
[1]*Department of Physics, Capital Normal University, Beijing 100048, People's Republic of China*
[2]*State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*
[3]*Beijing Institute of Aerospace Testing Technology, China Aerospace Science and Technology Corporation, Beijing 100074, People's Republic of China*

(Received 13 September 2013; accepted 22 October 2013; published online 6 November 2013)

Magnetic and magnetocaloric properties of $Dy_{12}Co_7$ compound have been investigated by magnetization measurements. Its magnetization does not reach saturation even for 7 T at 2 K due to the crystalline field effect. $Dy_{12}Co_7$ undergoes a ferromagnetic-paramagnetic phase transition around Curie temperature $T_C = 64$ K. The thermomagnetic irreversibility between the zero-field-cooling and field-cooling curves is detected below T_C in low magnetic field, and it is attributed to the narrow domain wall pinning effect. Large magnetic entropy change of 10.0 J kg^{-1} K^{-1} and refrigerant capacity of 299 J kg^{-1} for a magnetic field change of 0–5 T are found around T_C, resulting from the large change of magnetization during the magnetic phase transition. The nature of second-order phase transition for $Dy_{12}Co_7$ induces the complete reversibility of magnetic entropy change around T_C, which is very favourable for the application of magnetic refrigeration.
 [http://dx.doi.org/10.1063/1.4829281]

I. INTRODUCTION

Magnetic refrigeration based on magnetocaloric effect (MCE) of solid-state working substances has been proved to be an attractively alternative technology due to its higher energy-efficient and environment-friendly features as compared with the common gas-compression refrigeration technology widely in service.[1–3] Many materials with a first-order or second-order phase transition (SOPT) have been found to exhibit large MCEs, such as $Gd_5(Si, Ge)_4$,[4] $La(Fe, Si)_{13}$,[5,6] MnAs,[7,8] MnFe(P, As),[9] Ni_2MnGa,[10] Gd,[3] etc. Much attention has also been paid to the heavy rare earth (R) intermetallic compounds with a giant MCE and low-temperature phase transition for the purpose of magnetic refrigerant application due to their large magnetic moments.[11–14] Currently, researches are still in progress for exploring new materials which have large MCE in the special working temperature range for the refrigeration technological application.

$R_{12}Co_7$ (R = Gd-Er) compounds crystallize in a monoclinic $Ho_{12}Co_7$-type structure ($P2_1/c$).[15] Recently, magnetic properties and MCEs of $Gd_{12}Co_7$, $Tb_{12}Co_7$, $Gd_{12-x}Tb_xCo_7$, and $Ho_{12}Co_7$ compounds have been reported.[16–19] $Gd_{12}Co_7$ undergoes a ferromagnetic (FM)-paramagnetic (PM) phase transition at Curie temperature $T_C = 163$ K as well as a spin-reorientation transition at 123 K. Both of $Gd_{12-x}Tb_xCo_7$ and $Tb_{12}Co_7$ exhibit only one FM-PM phase transition. Moreover, with the increasing substitution of Tb for Gd, the Curie temperature shifts toward low temperature and the corresponding MCEs around T_C gradually decreases. The peak values of magnetic entropy change ($-\Delta S$) are 4.6 J/kg K for $Gd_{12}Co_7$ and 3.08 J/kg K for $Tb_{12}Co_7$ for a field change of 0–2 T, respectively. Different from the aforementioned compounds, $Ho_{12}Co_7$ compound displays rich magnetic phase transition: antiferromagnetic (AFM)-AFM transition at $T_1 = 9$ K, AFM-FM transition at $T_2 = 17$ K, and FM-PM transition at $T_C = 30$ K. And correspondingly, two successive peaks of magnetic entropy change are shown. For a field change of 0–5 T, the maximum value of $-\Delta S \sim 19.2$ J/kg K is reported. According to these results, we can find that the variety of rare earth element greatly affects the magnetic properties and MCEs. How does the magnetic phase transition of $Dy_{12}Co_7$ compound evolve? Up to now, we have only seen the report about its crystalline structure. So in the present paper, the magnetic properties and MCEs of $Dy_{12}Co_7$ compound are investigated by magnetization measurements.

II. EXPERIMENTS

The $Dy_{12}Co_7$ ingot was prepared by arc melting Dy and Co with the purity better than 99.9 wt. % in a high-purity argon atmosphere. 5 at. % excessive Dy was used to compensate the weight loss during the arc melting. The melt-spun ribbons were obtained by using a single-roller melt-spinner at a cooper wheel surface speed of 50 m/s. A post-annealing of the products at 823 K for 72 h and then at 873 K for 72 h and a subsequent quenching to room temperature were performed to obtain crystalline samples. The crystalline structure of sample is determined by X-ray powder diffractometer. X-ray diffraction results indicate that the annealed ribbons are crystallized in a nearly single phase with a monoclinic $Ho_{12}Co_7$-type structure. The lattice parameters are found to be $a = 8.357$ Å, $b = 11.251$ Å, and $c = 13.907$ Å at room temperature, which are almost in agreement with the experimental results reported by Adams *et al.*[15] Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

[a)]Electronic mail: happylaugh746@gmail.com

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature (T) dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetization (M) under fields of 0.1 T and 2 T. In the ZFC mode, the sample was cooled to 5 K before the measuring field H was switched on and the measurement was made while warming up the sample to high temperature. After finishing the ZFC M-T measurement, we followed to take the data again in the presence of the same H while cooling the sample. This was the FC mode. One can find that $Dy_{12}Co_7$ experiences a FM-PM transition around the Curie temperature $T_C = 64$ K, defined as the minimum value of dM/dT curve. It can also be seen from Fig. 1 that the ZFC and FC curves are completely reversible in the vicinity of T_C as shown usually in magnetic materials with a second-order magnetic transition. Meanwhile, a significant thermal irreversibility between the ZFC and FC branches is clearly observed below T_C under 0.1 T. Like many rare earth-metal compounds,[20] $Dy_{12}Co_7$ may have strong anisotropy due to its large Dy content. It has been reported that in materials with high anisotropy energy and low exchange energy (which will be embodied by the low ordering temperature), the domain wall width could be comparable to that of lattice spacing, thus leading to a large pinning effect.[20,21] Considering the magnetic anisotropy and low T_C for $Dy_{12}Co_7$, the thermomagnetic irreversibility is likely attributed to the narrow domain wall pinning effect. When the sample is cooled under a zero field, it freezes in an irregular domain structure where the direction of the spontaneous magnetization is only determined locally by the magnetic anisotropy. When a small field is switched on and the sample is warmed up, the walls begin to move and in every domain the direction of magnetization turns into the energetically most favourable direction which now also depends on the direction of the applied field.[22] So we can see that the ZFC magnetization is low below T_C and reaches a maximum at low temperature. Whereas in FC mode, the magnetic field during the cooling prevents the pinning effect, and therefore the magnetization at low temperature is higher than that in ZFC mode and gradually reaches saturation.

The inset of Fig. 1 displays the temperature dependence of the reciprocal magnetic susceptibility χ^{-1} for $Dy_{12}Co_7$ under the field of 2 T. The susceptibility above ~75 K obeys the Curie-Weiss law with an effective moment $\mu_{eff} = 11.0\,\mu_B$ per Dy atom and a paramagnetic Curie temperature $\theta_P = 48.8$ K. It is found that the value of μ_{eff} for $Dy_{12}Co_7$ is larger than the free-ion value for Dy^{3+} ion (10.6 μ_B), which may result from a small moment on Co as observed in $Ho_{12}Co_7$.[19]

Figure 2 depicts the magnetization versus magnetic field for $Dy_{12}Co_7$ at 2 K, 48 K, and 64 K. The magnetization does not reach saturation even for 7 T. The saturation magnetic moment per Dy atom is calculated to be 5.9 μ_B by using the magnetization under 7 T at 2 K, which is smaller than that expected for Dy^{3+} free ion saturated moment (10 μ_B). This may result from the crystalline field effect, further confirming the large anisotropy of $Dy_{12}Co_7$. One can find from Fig. 2 that the coercivity decreases rapidly with the increase of temperature. A large coercive field of 9.95 kOe for $Dy_{12}Co_7$ at 2 K is observed. However, it decreases to 0.18 kOe at 48 K. When a magnetic field much higher than the maximal coercive field is applied, the magnetic domains are similarly oriented along the applied magnetic field direction whether for ZFC mode or FC mode. Thus, one can only find a small discrepancy between the ZFC and FC M-T curves at low temperature in fields as high as 2 T (see Fig. 1). The coercivity at 64 K is only 3.95 Oe, showing the soft magnetism of $Dy_{12}Co_7$ around T_C. It is highly desired for magnetic refrigeration applications.

The isothermal magnetization curves as a function of magnetic field for $Dy_{12}Co_7$ were measured in applied fields of up to 7 T in the temperature range of 4–101 K. Fig. 3(a) shows the typical isothermal magnetization curves of $Dy_{12}Co_7$. One can find that the $Dy_{12}Co_7$ exhibits typical FM nature at temperatures lower than T_C. The Arrott-plots[23] around T_C are presented in Fig. 3(b). According to the Banerjee criterion,[24] a magnetic transition is expected to be

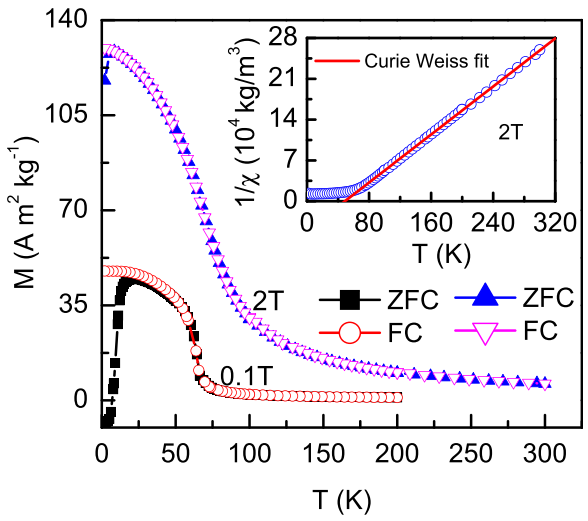

FIG. 1. Temperature dependences of ZFC and FC magnetization for $Dy_{12}Co_7$ under 0.1 T and 2 T. The inset shows the temperature variation of the ZFC inverse susceptibility fitted to the Curie-Weiss law under 2 T.

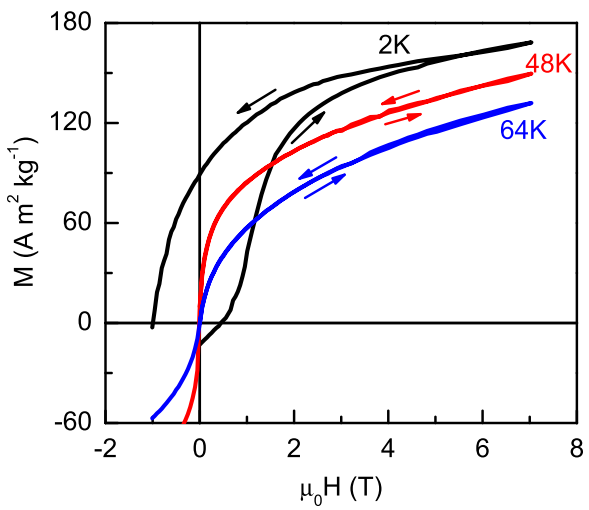

FIG. 2. Initial magnetization and demagnetization curves for $Dy_{12}Co_7$ at 2 K, 48 K, and 64 K.

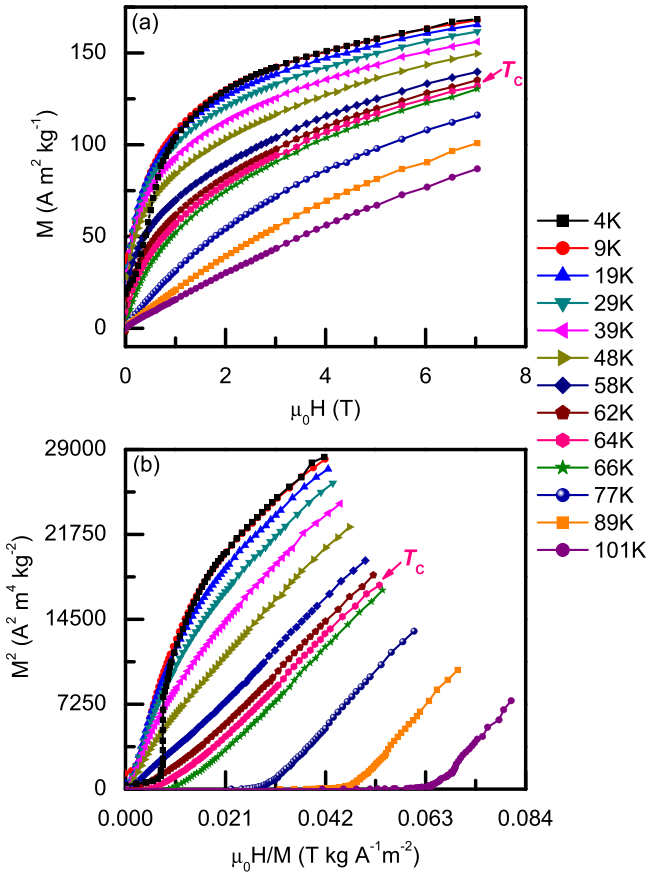

FIG. 3. Typical magnetic isothermals measured during field increasing (a) and Arrott-plots (b) of $Dy_{12}Co_7$.

of the first order when the slope of M^2 versus H/M plot is negative, whereas it will be of the second order when the slope is positive. It is very clear that the Arrott plot for $Dy_{12}Co_7$ indicates a characteristic of second-order magnetic transition.

The magnetic entropy change ΔS of $Dy_{12}Co_7$ compound can be calculated from isothermal magnetization data by using Maxwell relation $\Delta S = \int_0^H (\partial M/\partial T)_H dH$. Figure 4 displays the values of $-\Delta S$ for $Dy_{12}Co_7$ compound as a function of temperature for the typical field changes. The distinct "λ"-type of $-\Delta S$-T curves as well as the immovable position of the peak of $-\Delta S$ with the increase of field change further confirms the SOPT nature of $Dy_{12}Co_7$. The maximum values of $-\Delta S$ reach 4.9, 10.0, and 12.8 J kg^{-1} K^{-1} for the field changes of 0–2 T, 5 T, and 7 T, respectively. These values are comparable with or larger than those of some magnetocaloric materials with a SOPT in a similar temperature range under the same field change. For example, for the field change of 0–5 T, the maximum values of TbCoAl ($T_C = 70$ K),[11] $Er(Co_{0.85}Si_{0.15})_2$ ($T_C = 60$ K) (Ref. 25) are 10.5, and 8 J kg^{-1} K^{-1}, respectively. In addition, refrigerant capacity (RC), another important parameter to quantify the heat transferred between the hot and cold sinks in an ideal refrigeration cycle, is estimated by using the approach $RC = \int_{T_1}^{T_2} |\Delta S| dT$, where T_1 and T_2 are the temperatures corresponding to the both sides of half maximum value of $-\Delta S$ peak.[26] Thus, the RC values are obtained to be 83, 299, and, 473 J kg^{-1} for the field changes of 0–2 T, 5 T, and 7 T, respectively.

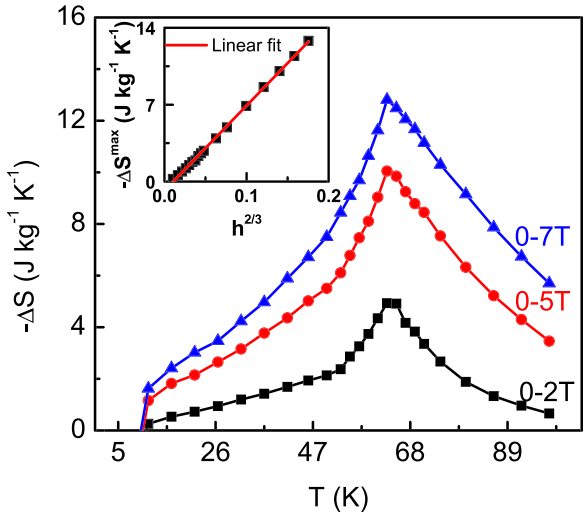

FIG. 4. Magnetic entropy change as a function of temperature for $Dy_{12}Co_7$ for magnetic field changes of 0–2 T, 0–5 T, and 0–7 T, where the inset shows the maximum isothermal magnetic entropy change as a function of $h^{2/3}$ at T_C, the solid line is the fitting one according to Eq. (5) in Ref. 28.

The linear relationship between $-\Delta S$ and $H^{2/3}$ is first predicted by Oesterreicher and Parker.[27] Recently, the relationship is discussed intensively by the renormalized group theory and verified by the experimental results.[28] In order to find out the dependence of MCE on the applied field for $Dy_{12}Co_7$, the maximum value of $-\Delta S$ ($-\Delta S^{max}$) at T_C as a function of $h^{2/3}$ ($h = \frac{\mu_0 \mu_B H}{k_B T_C}$) is plotted in the inset of Fig. 4. It can be well fitted by Eq. (5) in Ref. 28. The value of parameters -S(0,1) and S(0,0) defined in Ref. 28 are 77 J/kg K and −0.82 J/kg K, respectively. The appearance of negative S(0,0) is associated to the nonsaturation of the sample.[29]

Recently, based on soft magnetic amorphous alloys and lanthanide-based crystalline materials, Franco *et al.* constructed theoretically and experimentally the universal curve of magnetic entropy change for magnetocaloric materials with a second order phase transition.[30,31] Now, we construct the universal curve of $Dy_{12}Co_7$ by using the method with two reference temperature points in Ref. 30. The magnetic

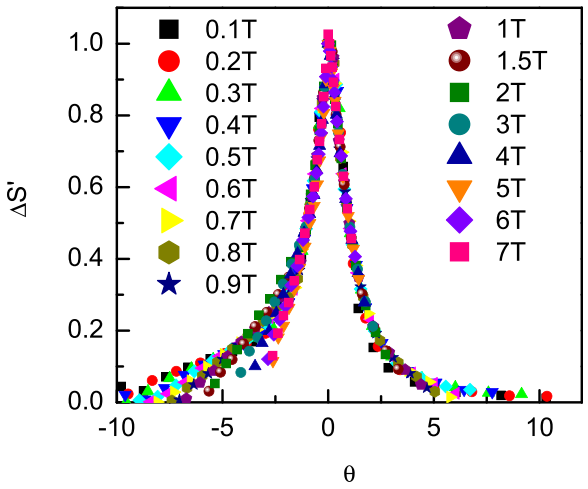

FIG. 5. Universal curve behavior of magnetic entropy change of $Dy_{12}Co_7$ for maximum applied fields ranging from 0.1 T to 7 T.

entropy change has to be rescaled to $\Delta S'(T, H_{max}) = \Delta S'(T, H_{max})/\Delta S^{max}(H_{max})$. The temperature axis has to be rescaled in a different way below and above T_C, just by imposing that the position of two additional reference points in the curve correspond to $\theta = \pm 1$

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C), & T \le T_C \\ (T - T_C)/(T_{r2} - T_C), & T > T_C, \end{cases} \quad (1)$$

where T_{r1} and T_{r2} are the temperatures of the two reference points that have been selected as those corresponding to $\frac{1}{2}\Delta S^{max}$. Figure 5 shows the θ dependence of $\Delta S'$ for typical field changes from 0.1 T to 7 T. The peaks of the curves collapse onto the same universal curve, which is associated with the second-order ferromagnetic ordering transition. While the low-temperature parts of the curves show tails, which may be associated with the large contribution of the crystalline electric field as discussed in $DyAl_2$ and $Er_{0.15}Dy_{0.85}Al_2$ compounds.[32]

IV. SUMMARY

$Dy_{12}Co_7$ undergoes a FM-PM transition around $T_C = 64$ K. The thermomagnetic irreversibility between ZFC and FC curves is detected below T_C in low magnetic field due to the narrow domain wall pinning effect. The large change of magnetization during the phase transition leads to large MCE. Large $-\Delta S$ of 10.0 J kg^{-1} K^{-1} and RC of 299 J kg^{-1} are found for a magnetic field change of 0–5 T. The result of Arrott-plots and the existence of the universal curve of $-\Delta S$ around T_C confirm the nature of second-order phase transition for $Dy_{12}Co_7$. The large and reversible magnetocaloric properties indicate the applicability of $Dy_{12}Co_7$ compound as a good candidate for magnetic refrigerant in middle-low temperature range.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51001077 and 11004204), the Hi-Tech Research and Development program of China, and the Beijing Excellent talent training support (Grant No. 2012D005016000002).

[1]E. Warburg, Ann. Phys. **249**, 141 (1881).
[2]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 (Institute of Physics Publishing, Bristol, 2003).
[3]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[4]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[5]F. X. Hu, B. G. Shen, J. R. Sun, and X. X. Zhang, Chin. Phys. **9**, 550 (2000).
[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]H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[8]S. Gama, A. A. Coelho, A. de Campos, A. M. G. Carvalho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004).
[9]O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).
[10]F. X. Hu, B. G. Shen, and J. R. Sun, Appl. Phys. Lett. **76**, 3460 (2000).
[11]X. X. Zhang, F. W. Wang, and G. H. Wen, J. Phys.: Condens. Matter **13**, L747 (2001).
[12]N. A. De Oliveira, P. J. Von Ranke, M. V. T. Costa, and A. Troper, Phys. Rev. B **66**, 094402 (2002).
[13]B. Li, J. Du, W. J. Ren, W. J. Hu, Q. Zhang, D. Li, and Z. D. Zhang, Appl. Phys. Lett. **92**, 242504 (2008).
[14]Q. Y. Dong, B. G. Shen, J. Chen, J. Shen, and J. R. Sun, J. Appl. Phys. **105**, 113902 (2009).
[15]W. Adams, J. M. Moreau, E. Parthé, and J. Schweizer, Acta Crystallogr. B **32**, 2697 (1976).
[16]J. Q. Deng, Y. H. Zhuang, J. Q. Li, and J. L. Huang, Physica B **391**, 331 (2007).
[17]X. Chen and Y. H. Zhuang, Solid State Commun. **148**, 322 (2008).
[18]Z. G. Zheng, X. C. Zhong, H. Y. Yu, Z. W. Liu, and D. C. Zeng, J. Appl. Phys. **109**, 07A919 (2011).
[19]X. Q. Zheng, X. P. Shao, J. Chen, Z. Y. Xu, F. X. Hu, J. R. Sun, and B. G. Shen, Appl. Phys. Lett. **102**, 022421 (2013).
[20]K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1977).
[21]J. L. Wang, C. Marquina, M. R. Ibarra, and G. H. Wu, Phys. Rev. B **73**, 094436 (2006).
[22]G. Ehlers, D. Ahlert, C. Ritter, W. Miekeley, and H. Maletta, Europhys. Lett. **37**, 269 (1997).
[23]A. Arrott, Phys. Rev. **108**, 1394 (1957).
[24]S. K. Banerjee, Phys. Lett. **12**, 16 (1964).
[25]N. H. Duc, D. T. K. Anh, and P. E. Brommer, Physica B **319**, 1 (2002).
[26]K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, and C. B. Zimm, Mater. Sci. Forum **315–317**, 69 (1999).
[27]H. Oesterreicher and F. T. Parker, J. Appl. Phys. **55**, 4334 (1984).
[28]Q. Y. Dong, H. W. Zhang, J. L. Shen, J. R. Sun, and B. G. Shen, J. Magn. Magn. Mater. **319**, 56 (2007).
[29]Q. Y. Dong, H. W. Zhang, J. R. Sun, B. G. Shen, and V. Franco, J. Appl. Phys. **103**, 116101 (2008).
[30]V. Franco, J. S. Blázquez, and A. Conde, Appl. Phys. Lett. **89**, 222512 (2006).
[31]V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, Annu. Rev. Mater. Res. **42**, 305 (2012).
[32]V. Franco, A. Conde, V. K. Pecharsky, and K. A. Gschneidner, Jr., Europhys. Lett. **79**, 47009 (2007).