Magnetocaloric response of FeCrB amorphous alloys: Predicting the magnetic entropy change from the Arrott–Noakes equation of state

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The magnetic entropy change in $Fe_{92-x}Cr_8B_x$ ($x=12,15$) amorphous alloys has been studied. Increasing the B content, both the peak entropy change and the Curie temperature of the alloy increase. This is in agreement with an increase in the average magnetic moment per iron atom. The thermal and field dependences of the magnetic entropy change curves have been analyzed with the use of the Arrott–Noakes equation of state. It is shown that determining the parameters in this equation of state (through fitting the magnetization data) allows prediction of the field and temperature dependences of the magnetic entropy change curves in a broad temperature range around the Curie temperature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2961310]

I. INTRODUCTION

The study of the magnetocaloric effect (MCE) with the aim of its application for near-room-temperature magnetic refrigeration has been revitalized since the discovery of the giant MCE (GMCE) in the past decade of the previous century.[1] Almost simultaneously, the demonstration of the feasibility of the application of this effect, not only at temperatures at the order of 10 mK (Ref. 2) but at temperatures that can be adequate for domestic appliances,[3] has fostered this line of research. The reasons for this increasing interest are the larger energetic efficiency of magnetic refrigerators (when compared with conventional ones based on the compression/expansion of gases) and the environmental benefits associated with the absence in the system of ozone depleting or greenhouse associated gases.

In recent years, there have been numerous attempts to enhance the magnetocaloric response of materials, and a number of excellent review papers[4–7] and books[8,9] have been published. The reduction of material costs, a requisite for the effective commercial application of the technology, is being achieved by replacing rare earths by transition metal based alloys.[10,11] However, in order to be able to apply a specific material to a real refrigerator, there are additional requisites that have to be considered: reduced hysteresis,[12] enhanced mechanical properties, and corrosion resistance.[13] The selection of a particular type of material for its application is also associated with a relevant decision: the selection of materials with a second order magnetic phase transition (MCE materials) or with a first order magnetostructural phase transition (GMCE materials). In the latter case, the peak magnetic entropy change ΔS_M^{pk} is larger, but the peak is also narrower in temperature than for the second order phase transitions. For a magnetic refrigerant material, a peak magnitude versus a peak width trade-off is necessary. Apart from the optimiza-

tion of material properties for quasistatic characterization (the one usually performed in research laboratories), it has to be taken into account that the cooling power of a magnetic refrigerator is a product of the operation frequency and of the quantity and relative cooling power of the refrigerant. Therefore, although materials with a second order phase transition may have a smaller ΔS_M^{pk}, this can be compensated by their faster response due to the lack of hysteresis, which can facilitate the increase in the operation frequency in refrigerator appliances.[14] Mainly because of all these requisites, present refrigerator prototypes still employ almost exclusively MCE materials with a second order magnetic phase transition (versus GMCE materials with a first order magnetostructural phase transition).

In particular, there is a growing interest in studying the applicability of soft magnetic amorphous alloys as magnetic refrigerants[15–27] due to their reduced magnetic hysteresis (virtually negligible), higher electrical resistivity, which would decrease eddy current losses (although current refrigerator prototypes are working at very low frequencies, recent theoretical calculations[14] predict operating frequencies in the 0.5 kHz range, which could make these losses more relevant), and tunable Curie temperature T_C. Nanoperm-type alloys are among the rare earth free soft magnetic amorphous alloys that currently exhibit the highest refrigerant capacity (RC) values, while the corresponding values of $|\Delta S_M^{pk}|$ still remain among the higher.[28] Corrosion resistance of the alloys can be enhanced by Cr alloying,[29,30] facilitating their applicability. Recently, it has been shown that tuning the Curie temperature (T_C) of the alloys by changing the Fe/B ratio may have the simultaneous effect of maintaining a constant magnetocaloric response of the alloy series.[26] As composites with a constant entropy change between the hot and cold reservoirs have been considered among the optimum materials for active magnetic regenerative refrigerators,[31,32] such

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materials with a constant value of $|\Delta S_M^{pk}|$ and different Curie temperatures could be a good starting point for the development of such composites.

From a practical point of view, the study of the field dependence of the magnetic entropy change has also attracted scientific interest.[33] As the performance of a magnetic refrigerator depends on the maximum applied field, the analysis of this field dependence for different types of materials can give further clues on how to improve the performance of refrigerant materials for the magnetic field range employed in actual refrigerators (generally 10–20 kOe). These studies have been made either experimentally[34–36] or from a theoretical point of view by restricting the description to a mean field approach.[37,38] Landau theory of magnetic phase transitions has also been employed to analyze the behavior of some specific materials.[39,40] More recently, the limitation of a mean field approach has been overcome by using the equation of state for materials with a second order magnetic phase transition.[41] Expressing the field dependence as $\Delta S_M \propto H^n$, this approach allowed us to find a relationship between the exponent n and the critical exponents of the material and to propose a phenomenological universal curve for the field dependence of ΔS_M, which was successfully tested for different series of soft magnetic amorphous alloys[28,41] and lanthanide based crystalline materials.[42,43] Although there is no closed analytical expression that can be fitted to the universal curve, there is a recent approach that allows describing the regions close to the peak with the help of a Lorentz function, which can be used by engineers as a tool in the design of refrigerator prototypes.[43] All these approaches put stress on describing the universal features of the ΔS_M curves, in some cases using the critical exponents, leaving aside the connection between the actual sample and this universal curve (associated with the critical amplitudes).

The purpose of this paper is twofold. On the one hand, the influence of the Fe/B ratio on the magnetocaloric response of an FeCrB amorphous alloy is analyzed. On the other hand, a study of the relationship between the parameters of the equation of state and the peak entropy change in the alloys is performed. It will be shown that in knowing these parameters, the value of $|\Delta S_M^{pk}|$ can be predicted and the shape of the ΔS_M curve is properly reproduced in the neighborhood of the Curie temperature; i.e., it gives the connection between the universal curve and the peculiarities of the ΔS_M curve of a particular sample.

II. EXPERIMENTAL

Amorphous ribbons ($\sim$1 mm wide and 10–20 μm thick) of $Fe_{92-x}Cr_8B_x$ ($x=12,15$) were obtained by melt spinning. Throughout this paper, the samples will be denoted as B12 and B15. The amorphous character of the as-quenched alloys was checked by x-ray diffraction. The thermal stability of the alloys against nanocrystallization has been studied by differential scanning calorimetry (DSC). The devitrification of the alloy takes place in two main stages, as evidenced by the DSC exotherms of Fig. 1 measured at 20 K/min. Increas-
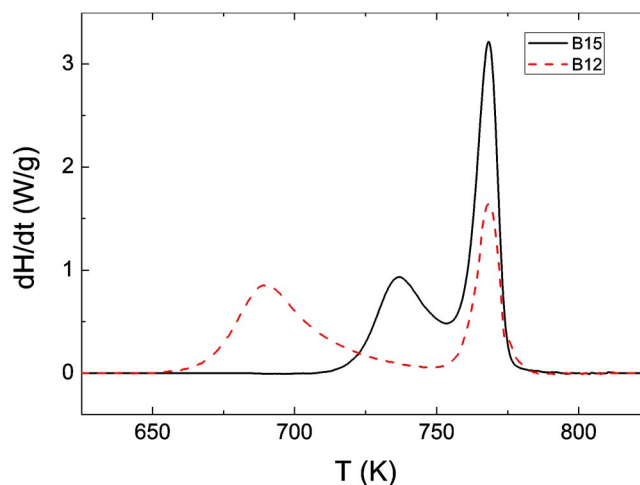

FIG. 1. (Color online) DSC records for the studied alloys measured at a heating rate of 20 K/min.

ing the B content in the alloy causes the onset temperature of the nanocrystallization process to shift from $\sim$663 K for the B12 alloy to $\sim$720 K for the B15 alloy.

The low temperature magnetic measurements were performed using superconducting quantum interference device (SQUID) magnetometry (Quantum Design MPMS-5S). The field dependence of magnetization was measured using a LakeShore 7407 vibrating sample magnetometer (VSM) using a maximum applied field $H=15$ kOe. The magnetic entropy change due to the application of the magnetic field H has been evaluated from the processing of the temperature and field dependent magnetization curves,

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \tag{1}$$

Prior to the measurements, the stress of the samples was relaxed by preheating them up to 525 K at a rate of 10 K/min.

The low temperature (5 K) magnetic moments of the studied alloys were 125.2 and 144.5 emu/g for the B12 and B15 alloys, respectively. These values correspond to average magnetic moments of Fe ($\langle\mu_{Fe}\rangle$) of $1.41\mu_B$ and $1.64\mu_B$, respectively. This increase in the average magnetic moment per Fe atom with increasing B content in the alloy is also a general feature for $Fe-ET-B$ ($ET=$Zr, Mo, etc.) alloys with low B content.[44]

III. RESULTS AND DISCUSSION

A. Compositional dependence of the magnetocaloric response

The magnetic entropy change in the studied alloys is presented in Fig. 2. There, the results of the high temperature measurements in the VSM are compared with the low temperature SQUID measurements, with a temperature region that has been measured in both pieces of equipment to allow for overlapping of the results. The small discrepancies when combining the VSM and SQUID results may emerge from the different field and temperature calibrations in both cases. It is also worth mentioning that the discretization of the tem-
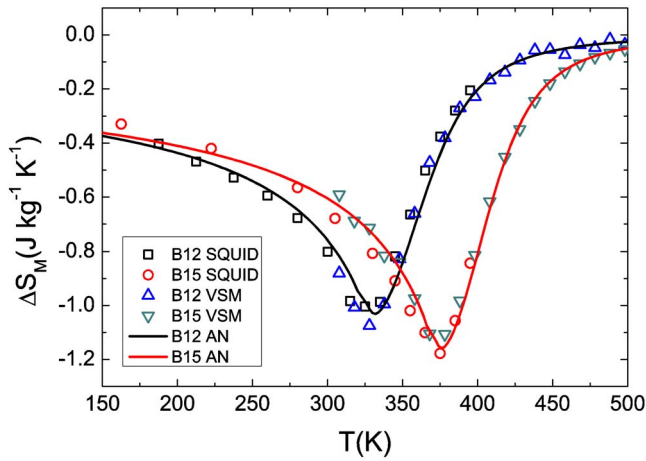
FIG. 2. (Color online) Symbols: Experimental values of the magnetic entropy change calculated from the VSM and SQUID magnetization data ($H = 1.5$ T) for the studied alloys. Solid lines: Predicted magnetic entropy change curves calculated from the magnetization curves fitted to the Arrott–Noakes equation of state.

perature axis (every 10 K in the present case) can also cause small differences in the experimentally determined $|\Delta S_M^{pk}|$. These differences remain below 7% (i.e., below the usually accepted error margin of this experimental determination of ΔS_M, which can be even above 10% according to several authors).[45] Despite this, it can be seen that $|\Delta S_M^{pk}|$ increases with increasing B content in the alloy. This increase can be more easily detected with measurements at higher applied fields, as evidenced in Table I. As in previous studies of the influence of the Fe/B ratio on the MCE of FeMoCuB amorphous alloys,[26] the present FeCrB alloy series evidences an increasing $|\Delta S_M^{pk}|$ with increasing average magnetic moment per Fe atom (which increases with increasing B content as indicated previously). However, there are two important differences with respect to the previous results, which have to be remarked: First, in the present case the peak entropy change does not remain constant when the Curie temperature of the alloy is displaced by B addition, which can be detrimental for their application as constituents of a composite material for Ericsson-type refrigerators. Second, although $|\Delta S_M^{pk}|$ increases with $\langle \mu_{Fe} \rangle$, this cannot be the only relevant

parameter, as in that hypothetical case the value of $|\Delta S_M^{pk}|$ for the B12 alloy should be below those of $Fe_{91-x}Mo_8Cu_1B_x$ ($x = 17, 20$), and this is not the case.[26]

In order to advance in the study of the material's parameters which control the actual magnetocaloric response of a particular alloy, we have to select a particular equation of state to be able to make analytical calculations. Recently it has been shown that the Arrott–Noakes equation of state is able to reproduce the shape of the universal curve of the MCE for amorphous alloys.[46] Therefore, we will make this particular choice to analyze the magnetic response of each of the samples.

B. Predicting the magnetic entropy change from the Arrott–Noakes equation of state

Let us consider that the magnetic equation of state of such a ferromagnetic material in the proximity of the transition temperature can be approximately described using the Arrott–Noakes equation of state,[47] which can be written as

$$H^{1/\gamma} = a(T - T_C)M^{1/\gamma} + bM^{1/\beta + 1/\gamma}, \qquad (2)$$

where β and γ are the critical exponents. For a given universality class (i.e., fixed values of the critical exponents), the differences from one material to the other can only come from the T_C and the parameters a and b. Taking into account that the critical exponents have to be determined from experimental results close to the critical region, an attempt to fit in one single step all the $M(H,T)$ data to Eq. (2) could give results that are far from physically reasonable. Therefore, the fitting procedure has been performed in two steps. First, the Curie temperature and the exponents β and γ have been determined in the following way. The extrapolation of the high field portion of the $M^{2.5}$ versus $(H/M)^{0.75}$ curves (Arrott–Noakes plot) was used to obtain the spontaneous magnetization and initial susceptibility from the intercepts with the $(H/M)^{0.75} = 0$ and $M^{2.5} = 0$ axes, respectively. These values were subsequently processed following the Kouvel–Fisher method[48] (the case for the B15 alloy is shown in Fig. 3) to obtain the critical exponents and a consistent determination of T_C. The results were $\beta = 0.46 \pm 0.01$ and $\gamma = 1.56 \pm 0.01$ for both alloys, and $T_C = 325 \pm 2$ K and $T_C = 370 \pm 1$ K for the B12 and B15 alloys, respectively. The

TABLE I. Experimental values of low temperature average magnetic moment per Fe atom, peak temperature and peak entropy change measured in the VSM or the SQUID, parameters a and b in the Arrott–Noakes equation of state derived from the fitting procedure, *prefactor*: field independent term of the magnetic entropy change at the Curie point [Eq. (4)], and predicted values of the magnetic entropy change at the Curie temperature by introducing in Eq. (4) the results of the fittings. For comparison, results for the FeMoCuB alloy series of Ref. 26 are also presented.

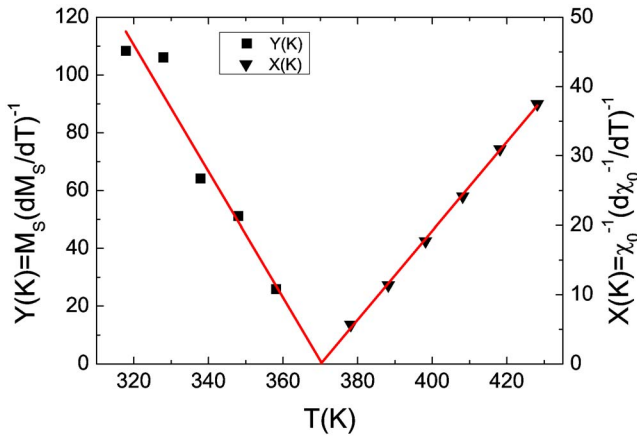|	T_{pk} (K)	$\langle \mu_{Fe} \rangle$ (μ_B)	$\|\Delta S_M^{pk}\|$ (J kg^{-1} K^{-1}) VSM ($H=1.5$ T)	$\|\Delta S_M^{pk}\|$ (J kg^{-1} K^{-1}) SQUID ($H=1.5$ T)	$\|\Delta S_M^{pk}\|$ (J kg^{-1} K^{-1}) SQUID ($H=5$ T)	a (K^{-1})	b (emu/g)$^{-1/\beta}$	Prefactor	$\|\Delta S_M(T_C)\|$ (J kg^{-1} K^{-1}) Predicted ($H=1.5$ T)	$\|\Delta S_M(T_C)\|$ (J kg^{-1} K^{-1}) Predicted ($H=5$ T)
$Fe_{80}Cr_8B_{12}$	328	1.41	1.07	1.00	2.59	1.166	8.60×10^{-3}	8.94	1.01	2.44
$Fe_{77}Cr_8B_{15}$	375	1.64	1.11	1.18	2.98	1.228	7.70×10^{-3}	10.04	1.13	2.74
Relative change			4%	15%	13%			11%	11%	11%
Alloys of Ref. 26										
$Fe_{76}Mo_8Cu_1B_{15}$	316	1.38	0.92							
$Fe_{74}Mo_8Cu_1B_{17}$	346	1.43	0.93							
$Fe_{71}Mo_8Cu_1B_{20}$	386	1.45	0.92							

FIG. 3. (Color online) Determination of the critical exponents and Curie temperature for the B15 alloy using the Kouvel–Fisher method.

values of the critical exponents are inside the range of those found for other amorphous alloys.[49] The second step in the fitting procedure consists of making the nonlinear fit of the experimental data to the surface

$$T = T_C + \frac{H^{1/\gamma} - bM^{1/\beta + 1/\gamma}}{aM^{1/\gamma}}, \qquad (3)$$

imposing the values of the Curie temperatures and critical exponents obtained in the previous step. The reason for selecting the temperature as the fitting variable is to avoid multivalued solutions of the equation, which could complicate the numerical procedure. The experimental results obtained from the VSM at fields ranging from 0.1 to 1.5 T have been used for the fitting. Some selected $M(T)$ data for different applied fields are presented in Fig. 4, together with the fitted curves. The parameters obtained in the fitting are presented in Table I.

By proper manipulation of the equation of state, an analytical expression for the magnetic entropy change at the transition temperature has recently been given as[41]

$$\Delta S_M|_{T=T_C} = \frac{-a\beta\gamma}{b^{(\beta+\gamma\beta)/(\beta+\gamma)}(2\beta+\gamma-1)} H^{(\beta-1)/(\beta+\gamma)+1}. \qquad (4)$$
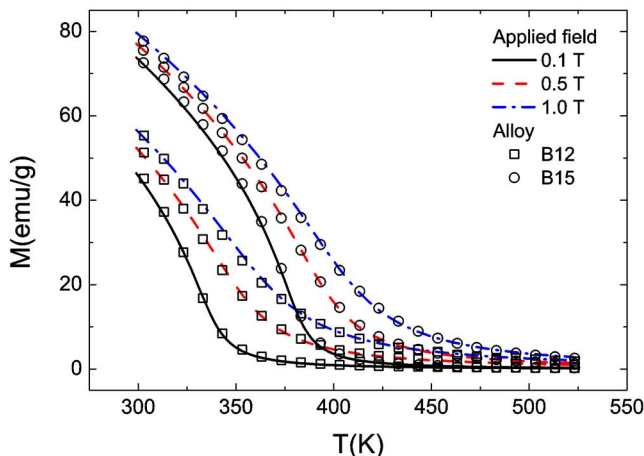

FIG. 4. (Color online) Symbols: Experimental VSM magnetization data for different applied fields. Lines: Fitting curves to the Arrott–Noakes equation of state.

This expression indicates that the field independent term in $\Delta S_M(T_C)$ (denoted as a prefactor in Table I) is completely determined by a, b, and critical exponents. Therefore, for a series of alloys of the same universality class, the differences in the magnitude of the $|\Delta S_M^{pk}|$ for each alloy should emerge from differences in a and b. There can be small differences between the predicted values using this equation and those of $|\Delta S_M^{pk}|$, which emerge from the fact that the temperature of the peak may be different from the Curie temperature (making $|\Delta S_M(T_C)| \leq |\Delta S_M^{pk}|$). However, these are outside the scope of this paper and will be studied elsewhere.[50] Nevertheless, these differences can be ruled out in the comparison if instead of comparing the values of $|\Delta S_M^{pk}|$ and $|\Delta S_M(T_C)|$ for each alloy, the relative change in these magnitudes for the two compositions are compared. The most reliable comparison in Table I is that of the 5 T SQUID data (since bigger differences are easier to resolve experimentally). Not only the values of $|\Delta S_M^{pk}|$ and of the predicted $|\Delta S_M(T_C)|$ are in good agreement but also the relative change in these magnitudes with changing compositions agrees.

However, knowing all the parameters appearing in the equation of state also allows predicting of the shape of the ΔS_M curves for the studied materials. The predicted curves have been calculated from the processing of the fitted magnetization curves and are plotted as continuous lines in Fig. 2. It is shown that for a relatively large temperature span around the Curie temperature (down to 170 K below T_C), the prediction of the Arrott–Noakes equation of state is rather accurate (the differences, with respect to the experimental data, are comparable to the differences between the SQUID and VSM data, i.e., the error margin).

IV. CONCLUSIONS

In conclusion, the magnetocaloric response of $Fe_{92-x}Cr_8B_x$ ($x=12,15$) alloys has been studied. The peak entropy change increases with the increasing average magnetic moment of Fe, i.e., increasing B content. However, in contrast to the results of the FeMoCuB alloy series, $|\Delta S_M^{pk}|$ does not remain constant when the Curie temperature is increased by increasing the B content. By fitting the experimental magnetization curves to the Arrott–Noakes equation of state, the parameters a and b, which control the differences between the values of $|\Delta S_M^{pk}|$ for both alloys, have been determined and the ΔS_M curves have been predicted. These predicted curves are in good agreement with the experimental results. This fitting procedure can be used to extrapolate the magnetocaloric response of materials for fields or temperatures that are not available in the laboratory.

ACKNOWLEDGMENTS

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[2] W. F. Giauque and G. P. MacDougall, Phys. Rev. **43**, 768 (1933).

[3] C. A. Zimm, A. Jastrab, A. Sternberg, V. K. Pecharsky, K. A. Gschneidner, Jr., M. G. Osborne, and I. E. Anderson, Adv. Cryog. Eng. **43**, 1759 (1998).

[4] K. A. Gschneidner, Jr. and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387 (2000).

[5] E. Bruck, J. Phys. D **38**, R381 (2005).

[6] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).

[7] A. M. Tishin, J. Magn. Magn. Mater. **316**, 351 (2007).

[8] A. M. Tishin, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1999), Vol. 12, pp. 395–524.

[9] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications* (Institute of Physics, Bristol, 2003).

[10] O. Tegus, E. Bruck, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).

[11] D. T. Cam Thanh, E. Brück, N. T. Trung, J. C. P. Klaasse, K. H. J. Buschow, Z. Q. Ou, O. Tegus, and L. Caron, J. Appl. Phys. **103**, 07B318 (2008).

[12] V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).

[13] V. Franco, C. F. Conde, A. Conde, and L. F. Kiss, Appl. Phys. Lett. **90**, 052509 (2007).

[14] M. D. Kuz'min, Appl. Phys. Lett. **90**, 251916 (2007).

[15] T. D. Shen, R. B. Schwarz, J. Y. Coulter, and J. D. Thompson, J. Appl. Phys. **91**, 5240 (2002).

[16] D. Wang, K. Peng, B. Gu, Z. Han, S. Tang, W. Qin, and Y. Du, J. Alloys Compd. **358**, 312 (2003).

[17] I. Škorvánek and J. Kováč, Czech. J. Phys. **54**, 189 (2004).

[18] S. Atalay, H. Gencer, and V. S. Kolat, J. Non-Cryst. Solids **351**, 2373 (2005).

[19] S. G. Min, K. S. Kim, S. C. Yu, H. S. Suh, and S. W. Lee, J. Appl. Phys. **97**, 10M310 (2005).

[20] V. Franco, J. S. Blázquez, C. F. Conde, and A. Conde, Appl. Phys. Lett. **88**, 042505 (2006).

[21] F. Johnson and R.D. Shull, J. Appl. Phys. **99**, 08K909 (2006).

[22] V. Franco, J. S. Blázquez, and A. Conde, J. Appl. Phys. **100**, 064307 (2006).

[23] V. Franco, J. M. Borrego, A. Conde, and S. Roth, Appl. Phys. Lett. **88**, 132509 (2006).

[24] V. Franco, J. M. Borrego, C. F. Conde, A. Conde, M. Stoica, and S. Roth, J. Appl. Phys. **100**, 083903 (2006).

[25] Q. Luo, D. Q. Zhao, M. X. Pan, and W. H. Wang, Appl. Phys. Lett. **89**, 081914 (2006).

[26] V. Franco, C. F. Conde, J. S. Blázquez, A. Conde, P. Švec, D. Janičkovič, and L. F. Kiss, J. Appl. Phys. **101**, 093903 (2007).

[27] J. Du, Q. Zheng, Y. B. Li, Q. Zhang, D. Li, and Z. D. Zhang, J. Appl. Phys. **103**, 023918 (2008).

[28] V. Franco, J. S. Blázquez, M. Millán, J. M. Borrego, C. F. Conde, and A. Conde, J. Appl. Phys. **101**, 09C503 (2007).

[29] F. F. Marzo, A. R. Pierna, A. Lorenzo, A. Altube, M. Sistiaga, A. Salaverría, and F. Fernández-Camacho, Mater. Sci. Forum **292–298**, 1047 (1998).

[30] A. Pardo, M. C. Merino, E. Otero, M. D. López, and A. M'hich, J. Non-Cryst. Solids **352**, 3179 (2006).

[31] C. E. Reid, J. A. Barclay, J. L. Hall, and S. Sarangi, J. Alloys Compd. **207–208**, 366 (1994).

[32] F. Shir, L. Yanik, L. H. Bennett, E. Della Torre, and R. D. Shull, J. Appl. Phys. **93**, 8295 (2003).

[33] A. M. Tishin, A. V. Derkach, Y. I. Spichkin, M. D. Kuz'min, A. S. Chernyshov, and K. A. Gschneidner, Jr., and V. K. Pecharsky, J. Magn. Magn. Mater. **310**, 2800 (2007).

[34] V. K. Pecharsky and K. A. Gschneidner, Jr., Adv. Cryog. Eng. **42**, 423 (1996).

[35] S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Rev. Sci. Instrum. **68**, 2432 (1997).

[36] F. Casanova, X. Batlle, A. Labarta, J. Marcos, L. Mañosa, and A. Planes, Phys. Rev. B **66**, 212402 (2002).

[37] H. Oesterreicher and F. T. Parker, J. Appl. Phys. **55**, 4334 (1984).

[38] For a comprehensive summary of the application to rare earth metals, see Sec. 8.1.8 of Ref. 9.

[39] A. Y. Romanov and V. P. Silin, Phys. Met. Metallogr. **83**, 111 (1997).

[40] V. S. Amaral and J. S. Amaral, J. Magn. Magn. Mater. **272–276**, 2104 (2004).

[41] V. Franco, J. S. Blázquez, and A. Conde, Appl. Phys. Lett. **89**, 222512 (2006).

[42] V. Franco, A. Conde, V. K. Pecharsky, and K. A. Gschneidner, Jr., Europhys. Lett. **79**, 47009 (2007).

[43] Q. Y. Dong, H. W. Zhang, J. R. Sun, B. G. Shen, and V. Franco, J. Appl. Phys. **103**, 116101 (2008).

[44] B. Yao, Y. Zhang, L. Si, H. Tan, and Y. Li, J. Alloys Compd. **370**, 1 (2004).

[45] V. K. Pecharsky and K. A. Gschneidner, Jr., J. Appl. Phys. **86**, 565 (1999).

[46] V. Franco, A. Conde, J. M. Romero-Enrique, and J. S. Blázquez, J. Phys. Condens. Matter **20**, 285207 (2008).

[47] A. Arrott and J. E. Noakes, Phys. Rev. Lett. **19**, 786 (1967).

[48] J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964).

[49] S. N. Kaul, J. Magn. Magn. Mater. **53**, 5 (1985).

[50] V. Franco, A. Conde, M. D. Kuzmin, and J. M. Romero-Enrique (unpublished).