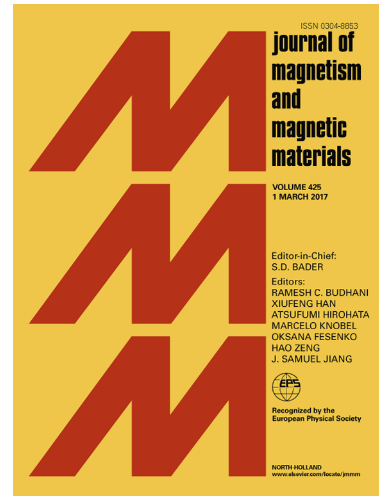
Journal Pre-proofs



Scaling analysis of phase transitions in magnetocaloric alloys

Roman Gozdur, Mariusz Najgebauer

PII: S0304-8853(19)32813-6
DOI: https://doi.org/10.1016/j.jmmm.2019.166239
Reference: MAGMA 166239

To appear in: *Journal of Magnetism and Magnetic Materials*

Received Date: 12 August 2019
Revised Date: 21 November 2019
Accepted Date: 28 November 2019

Please cite this article as: R. Gozdur, M. Najgebauer, Scaling analysis of phase transitions in magnetocaloric alloys, *Journal of Magnetism and Magnetic Materials* (2019), doi: https://doi.org/10.1016/j.jmmm.2019.166239

Scaling analysis of phase transitions in magnetocaloric alloys

Roman Gozdur[1] and Mariusz Najgebauer[2]

[1]*Lodz University of Technology, Department of Semiconductor and Optoelectronics Devices ul. Stefanowskiego 18/22, Poland, e-mail: roman.gozdur@p.lodz.pl*

[2]*Czestochowa University of Technology, Faculty of Electrical Engineering al. Armii Krajowej 17, 42-200 Częstochowa, Poland, e-mail: mariusz.najgebauer@pcz.pl*

Abstract. The paper presents magnetization measurements and the scaling analysis of related power loss for a high-temperature magnetocaloric alloy (T_C = 331 K). The measured hysteresis loops show anomalous behaviour near the temperature of 315 K, which may indicate the occurrence of additional phase transition. Power losses measured in different temperatures are analyzed using the scaling theory in order to determine the universal curves and the scaling exponents. The temperature dependence of scaling exponents confirms the existence of another phase transition at the temperature of 315 K, associated with an additional metallic phase in the alloy.

Key words: magnetocaloric materials; phase transitions; scaling analysis; magnetic power loss

1. Introduction

In recent years, a growing interest in the application of soft magnetic materials exhibiting magnetocaloric effect in room temperatures is observed. A significant part of research on the magnetocaloric effect and its application in magnetic refrigeration systems is motivated by greater efficiency of the magnetic cooling cycle and much more eco-friendly solutions [1-4]. However, taking into account all aspects of obtaining, production and recycling of magnetocaloric materials, it turns out that magnetic cooling systems are becoming uncompetitive in comparison with conventional cooling systems based on vapour-compression refrigeration [5]. Considering the cooling process as electrically forced heat transport and the related demand for electric energy, the issue of energy efficiency in the magnetic cooling systems remains as important as for all other electrical devices [6]. It should be noted that, according to the International Institute of Refrigeration, global demand for electricity related to cooling systems is 15% and a further increase of another 10% per year is expected [3]. By reducing the amount of energy dissipated in materials used for heat transport, the energy efficiency of cooling systems can be improved. This should reduce global electricity demand due to the huge number of refrigeration devices used around the world. For this reason, research and analysis of power losses in magnetocaloric materials, just like in conventional soft magnetic materials, are justified because magnetic power loss is immanent and associated with the alternating magnetic field needed to produce a thermomagnetic cycle.

The lack of standardization in the field of magnetocaloric components in magnetic refrigerators [7,8] as well as tools for their testing is the motivation to our research in this subject. This present paper is an attempt to adapt the scaling analysis, used previously in research of power loss in ferromagnetic materials, in order to investigate power loss in the Calvoric-type magnetocaloric alloy $La(Fe_xCo_ySi_{1-x-y})_{13}$ in the phase transition state. Validation of the scaling analysis in magnetocaloric materials should enable a more accurate research of their energy efficiency in the temperature range above room temperature at which these materials are most desirable.

It should be noted that magnetocaloric refrigeration technology is intensively developed, but there is no breakthrough in commercial applications, and the large number of announced magnetocaloric refrigerators are only laboratory prototypes [9-11]. However, exemplary progress in the development of Calorivac alloys, from Calorivac-C to Calorivac-H, strongly encourages the scientific community to continue working on magnetic refrigeration. Thus, this work can be a small step towards the commercial application of La-containing magnetocaloric materials.

2. Magnetocaloric samples and instrumentation

The test core used in the study was made as a set of four identical plates made of $La(Fe_xCo_ySi_{1-x-y})_{13}$ sintered solids manufactured by the Vacuumschmelze Company [8]. The elemental mapping carried out by the EDS method reveal high consistency of the element content in all four samples with nominal phase composition. Slight discrepancies occur locally in places where the continuity of the sintered structure has not been maintained. These are spreads in which local oxidation or crystallization of iron has occurred. Surface analysis of elements distribution does not indicate inhomogeneity (see Fig. 1) which could have are bulk, the existence of other metallic phases cannot be excluded.

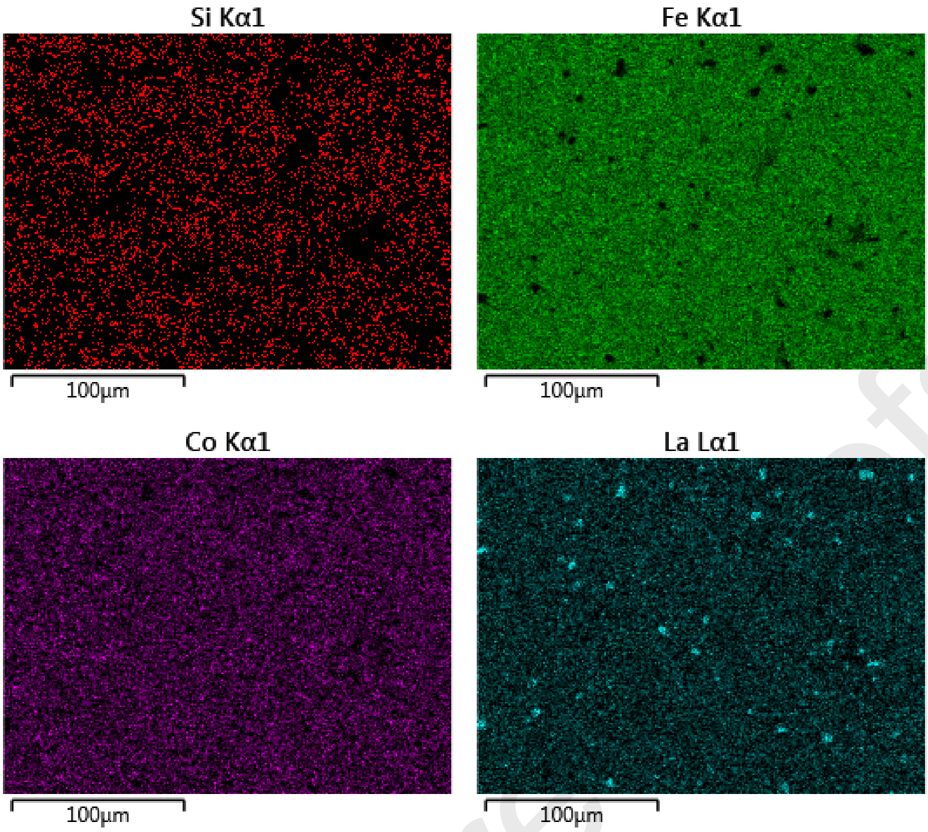


Fig. 1. Typical distribution of Si, Fe, Co, La elements from the EDS elemental mapping

Plate samples (36 × 18 × 5 mm), uncoated with a protective layer, were assembled in a non-magnetic measuring yoke, as depicted in Figure 2. The total core weight was 0.0950 kg. The average magnetic path was determined on the basis of core geometrical dimensions. Its value considered in further calculations was L_{MCE} = 0.149 m. The contact reluctance of the plates was significantly reduced by the high smoothness of the plates and the use of clamping screws at the corners of the magnetic circuit (Fig.2). The entire core was locally bonded with epoxy adhesive and enclosed in a thermostatic system. The thermostat operating range was from 280 K to 345 K with the accuracy of 0.1 K and the time constant of 1000 s. RTD temperature sensors in the form of PT100 thin-film (class A) were placed on two opposite sides of the core. Temperature measurements were carried out in a 4-wire connection system made using LTC2983 thermometers. The basic parameters of the tested magnetocaloric alloy are presented in Table 1 and depicted in Figure 3.

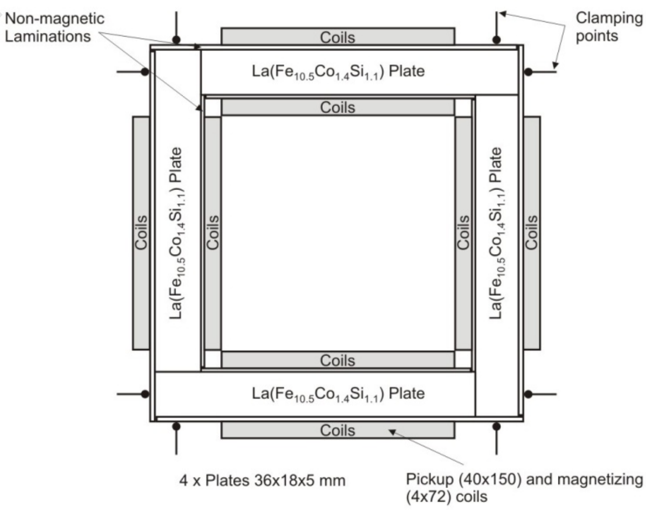


Fig.2. Diagram of assembled magnetocaloric core in the non-magnetic yoke

Composition $La(Fe_{10.5}Co_{1.4}Si_{1.1})$	
Max. entropy changes (111kA/m)	$\lvert \Delta S_M(T) \rvert$ = 34.4 kJ/m³K
Nominal Curie temperature	Tc = 330K
Temperature of peak entropy	T_{peak} = 328 K (H=111 kA/m)
Density	ρ = 7169 kg/m³

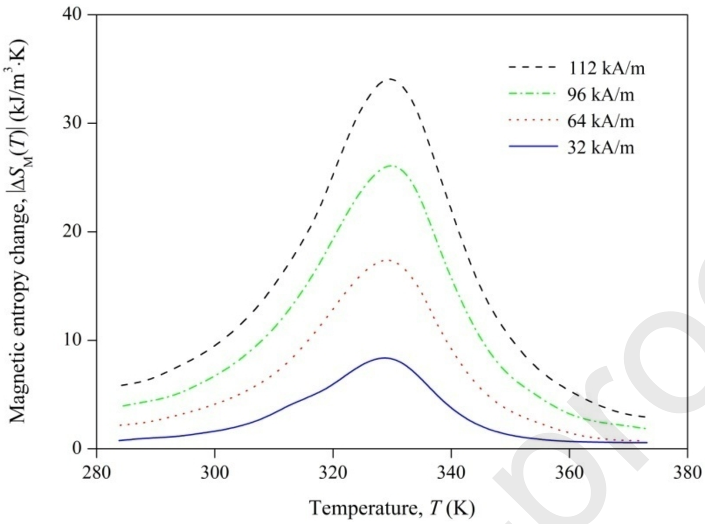


Fig.3. Influence of temperature and magnetic field strength on magnetic entropy changes of $La(Fe_{10.5}Co_{1.4}Si_{1.1})$ composition

Magnetic parameters of the magnetocaloric core was measured in the surrounding of the Curie temperature T_C = 330 K using the measuring system described in detail in [12,13]. The basic temperature relations $J_m(T)$, $J_r(T)$, $H_C(T)$ were determined on the basis of hysteresis loop measurements carried out at frequency of 1.0 Hz (Figure 4) and superimposed on the entropy changes $|\Delta S_M(T)|$ in the surrounding of phase transition (Figure 5). The presented results confirm the gradual disappearance of ferromagnetic properties near the temperature of 330 K.

A very important issue in magnetic property measurements is the appropriate shaping of electromotive force waveforms (*EMF*) in the measuring winding. However, in the temperature range from 315 K to 330 K, significant distortion of *EMF* waveforms can be observed, which begin to disappear at temperatures above 331 K, as depicted in Figure 6. These distortions may indicate phase transition occurring in this temperature range that prevent obtaining “smooth” waveforms of electromotive force.

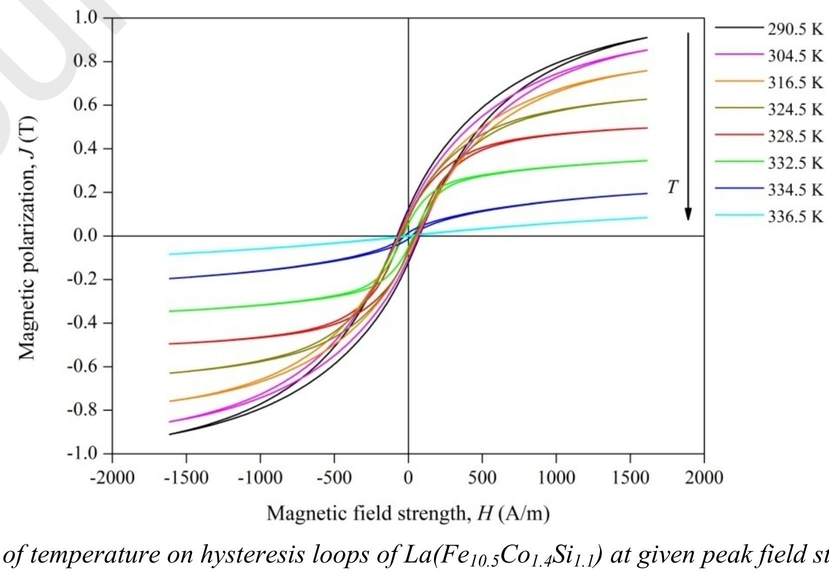


Fig.4. Influence of temperature on hysteresis loops of $La(Fe_{10.5}Co_{1.4}Si_{1.1})$ at given peak field strength 1600 A/m near the transition point (T_C = 330 K)

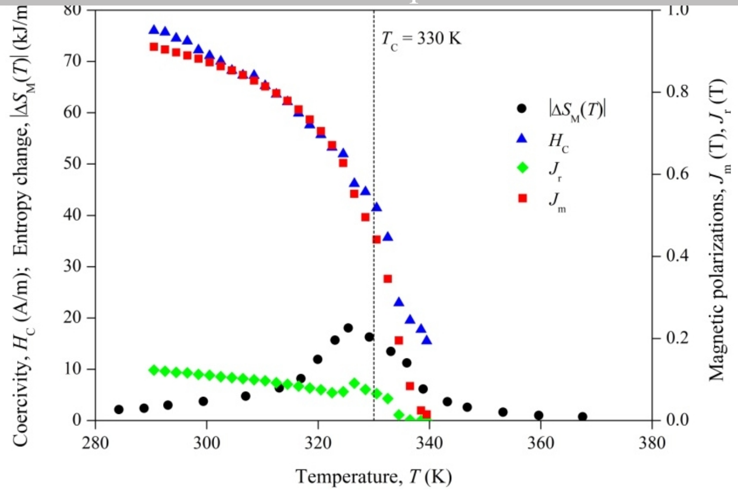


Fig.5. Magnetic properties of the La($Fe_{10.5}Co_{1.4}Si_{1.1}$) near the transition point (T_C = 330 K)

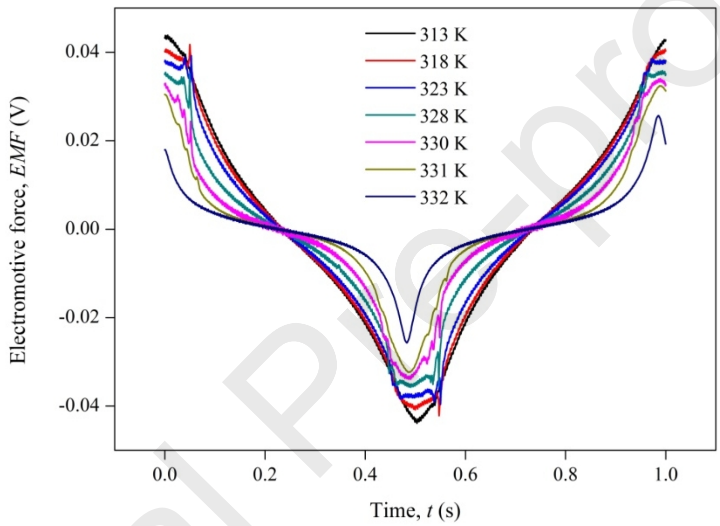


Fig.6. Waveforms of EMF(t) force at different temperatures

Analyzing the temperature influence on the hysteresis loop shape in the range up to 323 K, an anomalous behaviour can be also noticed. As the temperature rises, the slope of the hysteresis loop decreases (loop tips are reached for higher values of magnetic field strength), while at 315 K an abrupt change is observed. The slope of the hysteresis loop increases and then returns to the previous trend at 319 K, as depicted in Figure 7. This may indicate the occurrence of phase transition at 315 K, associated with magneto-structural changes in the alloy. However, the magneto-structural phase transition temperature is usually slightly lower than the ferro–paramagnetic transition temperature. In the analyzed case, this difference is 15 K, which indicates another source of the observed anomaly. Due to the fact that the sample is substantially a homogeneous alloy but it was created by high temperature sintering of fine particles, it is possible that an additional residual phase with a lower Curie temperature was created in the material. The existence of this phase may also be indicated by a slight deformation of entropy change curves (see Fig. 3) near a temperature of 315 K, visible especially for a low magnetic field of 32 A/m. This phenomenon will be investigated using the scaling analysis.

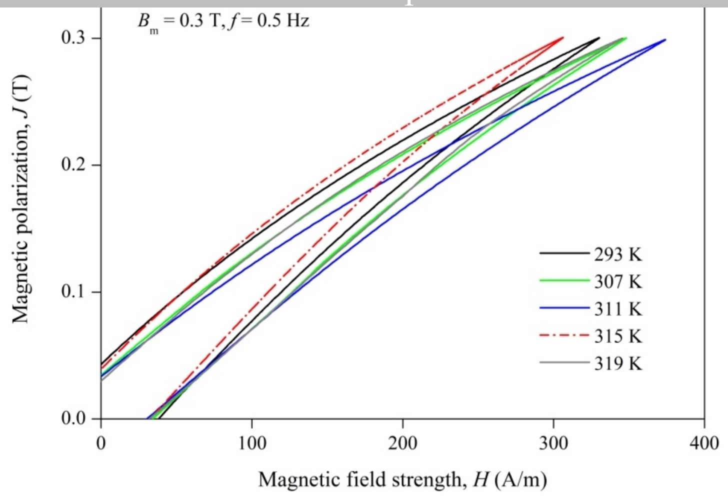


Fig.7. Temperature dependency of hysteresis loops

3. Scaling analysis in phase transitions

Phase transitions are thermodynamic processes associated with the transfer of substances from one thermodynamic phase to another. There are two types of phase transitions – the first and second order ones. The first order phase transition is characterized by a discontinuous change of the equation of state, whereas in the case of the second order phase transition – a change of the equation of state is continuous. The second order phase transitions are usually described by critical exponents, their relationships in the form of scaling laws and the universal equation of state, which are determined analytically using the scaling analysis [14,15].

In magnetocaloric alloys, first and second order phase transitions, e.g. ferro–paramagnetic (FM-PM) at the Curie temperature or antiferro–paramagnetic (AFM-PM) at the Néel temperature, can be observed. A theoretical analysis of the second order phase transition in these alloys has been presented in numerous papers [16-20]. An alternative, phenomenological method for analyzing the second order phase transition has been proposed by V. Franco's research team. In this method, a universal curve can be determined using only measurements, without *a priori* knowledge of critical exponents and the equation of state. The construction of the phenomenological universal curve is carried out in three steps: identification of the reference temperature; normalization of curves with respect to their maximum; rescaling the temperature axis. This method was successfully applied in investigations of the second order phase transitions for amorphous soft magnetic materials [21,22] and magnetocaloric alloys [23].

Another method of phenomenological determination of critical exponents and a universal curve is based on a homogenous function in the general sense. This function is defined as:

$$\exists(a_1, ..., a_n, b)\lambda^b f(x_1,..., x_n) = f(\lambda^{a_1}x_1,..., \lambda^{a_n}x_n), \tag{1}$$

where: f is a phenomenological equation of state x_1,..., x_n are independent variables, a_1, ..., a_n, b are scaling exponents and λ is a scaling factor [15]. It allows one to collapse a family of measured curves onto the universal curve in a two-step procedure: by selecting the appropriate scaling factor λ and estimating the scaling exponents from measurements.

This method and its extensions were successfully used in the analysis of energy dissipation for various soft magnetic materials in the room temperature range [24-29], and thus for phenomena distant from a second order phase transition. In these studies, the following phenomenological equation of state was assumed on the basis of loss measurements:

$$P_S = P(B_m, f), \tag{2}$$

where: P_S is specific power loss, B_m is a peak induction and f is magnetizing field frequency. By using the Eq. (1) and for the appropriately selected scaling factor λ, the phenomenological equation of state (2) can be easily transformed to the peak induction-scaled form:

$$P_{\mathrm{B}} = p_{\mathrm{B}}(f_{\mathrm{B}})^{x}, \tag{3}$$

or to the frequency-scaled form:

$$P_{\mathrm{f}} = p_{\mathrm{f}}(B_{\mathrm{f}})^{x}, \tag{4}$$

where: $P_{\mathrm{B/f}}$ is scaled specific loss, f_{B} is scaled frequency, B_{f} is scaled peak induction, $p_{\mathrm{B/f}}$ is a scaling function and x is a so-called fractional exponent [27].

4. Results and discussion

The hysteresis loop and $EMF(t)$ measurements presented in Section 2 indicate the anomalous behaviour of magnetization processes near the temperature of $T = 315$ K, which might be related to the existence of an additional phase in the alloy. This suggests that the scaling exponents should change their values in the surrounding of 315 K. This issue is investigated using the scaling analysis of specific power loss, determined from the area of the hysteresis loop. For this purpose, additional measurements were carried out, including hysteresis loop families measured under the following conditions: magnetizing frequency f = 0.5, 1, 2, 5, 10 Hz; peak induction $B_{\mathrm{m}} = 0.1 \ldots 0.9$ T (with step 0.1 T); temperature $T = 293$ K and 295 ... 323 K (with step 4 K).

The frequency-scaled equation of state (4) has the detailed form:

$$\frac{P_{\mathrm{S}}}{f^{\alpha}} = p \cdot \left(\frac{B_{\mathrm{m}}}{f^{\beta}}\right)^{x}, \tag{5}$$

where: α and β are scaling exponents, p is scaling coefficient. The α, β, p and x parameters are estimated using power loss measurements, carried out for all temperatures mentioned in Section 2, except $T = 331$ K due to technical limitations of the measuring system. Power loss curves measured at the room temperature are depicted in Figure 8a, whereas the corresponding universal curve obtained using the Eq. (5) is depicted in Figure 8b. The exemplary universal curves of loss measurements for temperature $T = 315$ K and $T = 323$ K are depicted in Figures 9 and 10, respectively. In the temperature range up to $T = 307$ K, the universal curves of loss measurements have almost the same shape. For temperatures $T = 311$, 315 and 319 K, the shape of the universal curves is slightly changed and the scaled-induction range is reduced, but the data collapse is still achieved. Whereas for temperature $T = 323$ K the collapse data of loss measurements is not fully obtained, which is probably due to the material approaching the second order phase transition.

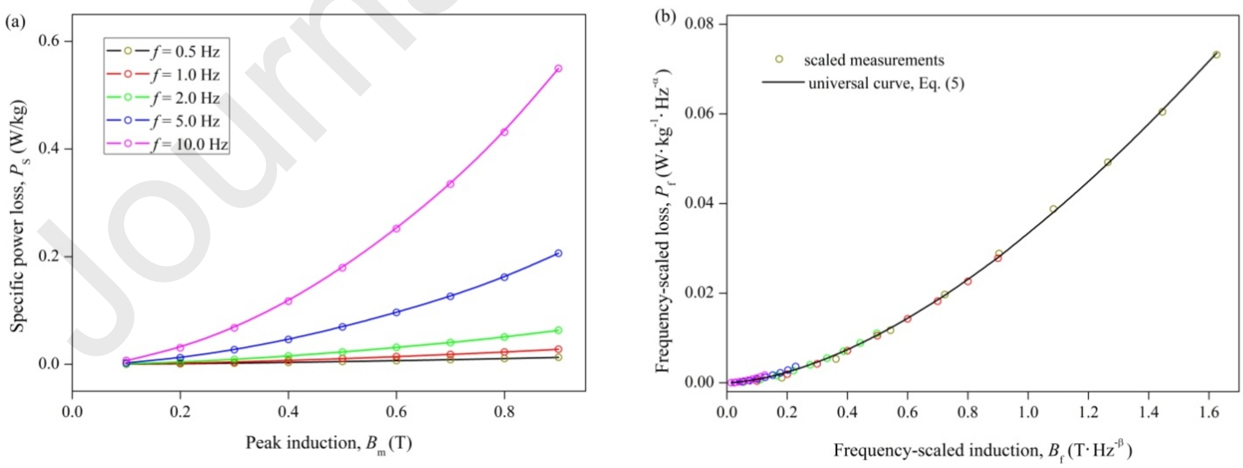


Fig.8. Power loss measurements (a) and the universal curve (b) for LaFeCoSi alloy at room temperature

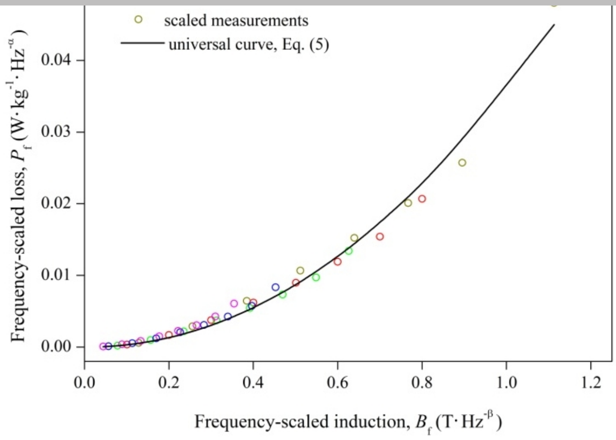


Fig.9. The universal curve of power loss at 315 K

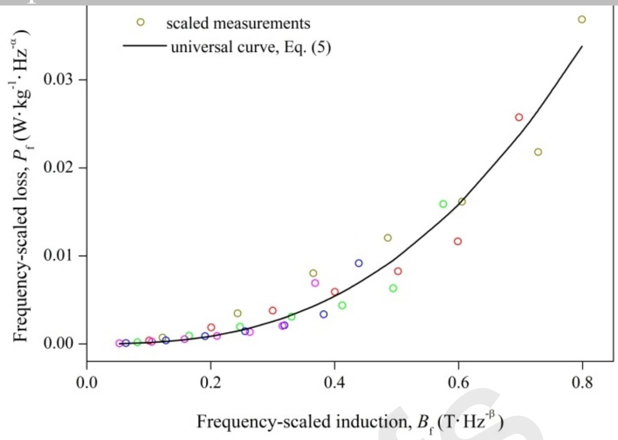


Fig.10. The universal curve of power loss at 323 K

The value of scaling parameters α, β and x are compared in Table 2 as well depicted in Figure 11. It should be noticed that the scaling parameters α and β have almost constant values for temperatures up to 307 K. As the temperature increases, their values decrease and reach the minimum for T = 315 K. Then the exponents increase to the previous values at T = 319 K and again decrease with further temperature increase. The exponent x also revealed a temperature dependence, but at T = 315 K it reaches the local maximum value. The changes in the value of scaling exponents indicates that the material belongs to different universality class, depending on the temperature. There is one universality class in the temperature range 293 – 307 K, while in the surrounding of T = 315 K and T = 323 K there may be changes in universality classes, related to various phase transitions.

Table 2. Values of the scaling parameters

T (K)	293	295	299	303	307	311	315	319	323
α	2.52	2.45	2.50	2.52	2.51	2.32	1.86	2.46	2.07
β	0.85	0.81	0.84	0.84	0.82	0.67	0.35	0.81	0.28
x	1.64	1.64	1.64	1.64	1.66	1.73	2.05	1.63	2.65

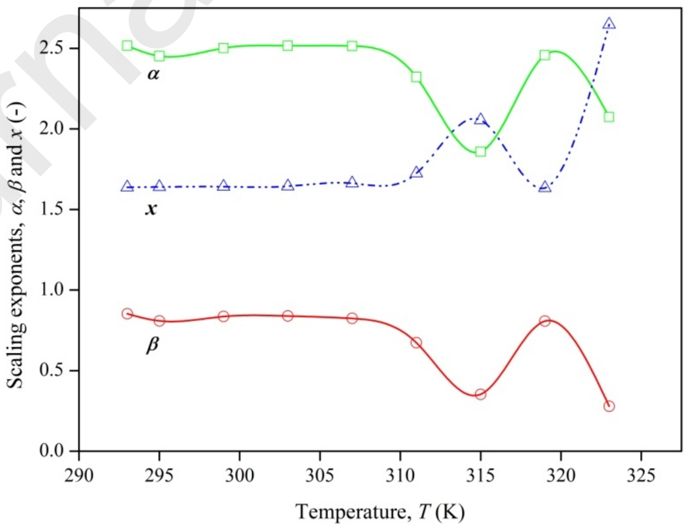


Fig.11. Temperature dependence of the scaling exponents α, β and x

The temperature dependency of the scaling exponents α, β and x is convergent with the observed behaviour of the magnetizing process. These results indicate that the examined alloy has a two-phase structure and the additional phase transformation, associated with the residual phase, occurs near 315 K. It should be noted that the proposed method is very sensitive, as it allows one to determine the temperature of the other hand, this method has been used so far to analyze physical phenomena associated with magnetization processes in soft magnetic materials such as coercivity [30], anisotropy [31] or magnetic hysteresis [32,33]. Thereby, the proposed scaling analysis can be considered as a general method that can be applied to analyze phase transitions in various magnetocaloric alloys.

5. Conclusions

Phase transitions are usually analyzed using the scaling theory to determine the universal equation of state, critical exponents and scaling laws. The paper presents an alternative approach to the analysis of phase transitions in magnetocaloric alloys, using phenomenological scaling based on a homogeneous function in the generalize sense. This approach was validated for a high-temperature magnetocaloric alloy $La(Fe_{10.5}Co_{1.4}Si_{1.1})$.

The scaling analysis allowed the initial determination of the phase transition temperature, associated with an additional metallic phase existing in the alloy. The values of the scaling exponents and the universal (data collapse) curve were determined using hysteresis and power loss measurements, carried out in a wide temperature range, in 4K increments. Both measured hysteresis loops as well as obtained temperature dependency of the scaling exponents indicated the occurrence of the phase transition near the temperature $T = 315$ K. A more accurate determination of the phase transition temperature and corresponding scaling exponents is possible, however, this requires additional measurements of loss curves, carried out in the surrounding of the pre-located phase transition temperature, but with much smaller temperature increments. Such measurements require a measuring system with very precise temperature stabilization.

Based on the obtained results, it can be concluded that the proposed scaling method allows the analysis of phase transitions in magnetocaloric alloys. This method shows high sensitivity, which is manifested by a significant change in the value of scaling parameters in the surrounding of phase transition temperatures. Thereby, it also allows to determine hardly noticeable phase transitions. The validation of this method for other magnetocaloric alloys as well as more accurate determination of transition temperatures will be a subject of further research.

Acknowledgements

The project financed under the program of the Minister of Science and Higher Education under the name "Regional Initiative of Excellence" in the years 2019–2022 project number 020/RID/2018/19, the amount of financing 12,000,000 PLN.

This research was partly supported by the National Science Centre of Poland, grant No. 4889/B/T02/2011/40.

References

[1] V. Franco, *et al.*, Prog. Mater. Sci. **93**, 112–232 (2018). DOI: 10.1016/j.pmatsci.2017.10.005
[2] M. Almanza, *et al.*, Eur. Phys. J. - Appl. Phys. **71** (1), 10903 (2015). DOI: 10.1051/epjap/2015150065
[3] B. Monfared and B. Palm, Int. J. Refrig. **96**, 25–37 (2018). DOI: 10.1016/j.ijrefrig.2018.08.012
[4] M. Balli, *et al.*, Appl. Phys. Rev. **41**, 21305–21302 (2017). DOI: 10.1063/1.4983612
[5] B. Monfared, R. Furberg, and B. Palm, Int. J. Refrig. **42**, 69–76 (2014). DOI: 10.1016/j.ijrefrig.2014.02.013
[6] O. Gutfleisch, *et al.*, Adv. Mater. **23** (7), 821–842(2011). DOI: 10.1002/adma.201002180
[7] B. Yu, *at al.*, Int. J. Refrig. **33** (6), 1029–1060 (2010). DOI: 10.1016/j.ijrefrig.2010.04.002
[8] M. Katter, *et al.*, IEEE Trans. Magn. **44** (11), 3044–3047 (2008). DOI: 10.1109/TMAG.2008.2002523
[9] Y. Miyazaki, *et al.*, QR of RTRI **55** (2), 119–124 (2014). DOI: 10.2219/rtriqr.55.119
[10] C. Zimm, *et al.*, Int. J. Refrig. **29** (8), 1302–1306 (2006). DOI: 10.1016/j.ijrefrig.2006.07.014
[11] M. Balli, *et al.*, Mat. Sci. Eng. B-ADV **177** (8), 629–634 (2012). DOI: 10.1016/j.mseb.2012.03.016
[12] R. Gozdur and M. Najgebauer, J. Electr. Eng. **66** (7/s), 37–40 (2015).
[13] R. Gozdur, Acta Phys. Pol. A **128** (1), 98–103 (2015). DOI: 10.12693/APhysPolA.128.98
[14] B. Widom, J. Chem. Phys. **43**, 3898–3905 (1965). DOI: 10.1063/1.1696618
[15] H.G. Stanley, Rew. Mod. Phys. **71** (2), S358–366 (1999). DOI: 10.1103/RevModPhys.71.S358
[16] V. Franco.,*et al.*, J. Phys.: Condens. Matter **20** (28), 285207 (2008). DOI: 10.1088/0953-8984/20/28/285207
[17] V. Franco, *et al.*, J. Magn. Magn. Mater. **322** (2), 218–223 (2010). DOI: 10.1016/j.jmmm.2009.08.039
[18] C.M. Bonilla, *et al.*, Phys. Rev. B **81**, 224424 (2010). DOI: 10.1103/PhysRevB.81.224424
[19] V. Franco, *et al.*, J. Appl. Phys. **109**, 07A905 (2011). DOI: 10.1063/1.3535191
[20] C. Romero-Muñiz, *et al.*, Phys. Rev. B, **94** 134401 (2011). DOI: 10.1103/PhysRevB.94.134401
[21] V. Franco, *et al.*, Appl. Phys. Lett. 89, 222512 (2006). DOI: 10.1063/1.2399361

[23] V. Franco and A.Conte, Int. J. Refrig. **33** (3), 465–473 (2010). DOI: 10.1016/j.ijrefrig.2009.12.019
[24] K.Z. Sokalski, *et al.*, COMPEL **26**, 640–649 (2007). DOI: 10.1108/03321640710751118
[25] B. Ślusarek, *et al.*, J. ALLOY. COMPD. **581**, 699–704 (2013). DOI: 10.1016/j.jallcom.2013.07.084
[26] A. Ruszczk, and K.Z. Sokalski, COMPEL **34** (1), 371–379 (2015). DOI: 10.1108/COMPEL-11-2013-0407
[27] M. Najgebauer, Acta Phys. Pol. A **128** (1), 107–110 (2015). DOI: 10.12693/APhysPolA.128.107
[28] M. Najgebauer, Acta Phys. Pol. A **131** (5), 1225–1227 (2017). DOI:10.12693/APhysPolA.131.1225
[29] M. Najgebauer, *et al.*, COMPEL **38** (4), 1064–1074 (2019). DOI: 10.1108/COMPEL-10-2018-0412
[30] M. Najgebauer, Acta Phys. Pol. A **113** (4), 633–635 (2017). DOI: 10.12693/APhysPolA.131.633
[31] M. Najgebauer, Archives **66** (2), 423–432 (2017). DOI: 10.1515/aee-2017-003
[32] K.Z. Sokalski, Acta Phys. Pol. **127** (3), 850–853 (2015). DOI: 10.12693/APhysPolA.127.850
[33] M. Najgebauer, Physica B **577**, 411765 (2020). DOI: 10.1016/j.physb.2019.411765

CRediT author statement

Roman Gozdur: Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data Curation, Writing - Original Draf, Writing - Review & Editing, Funding acquisition

Mariusz Najgebauer: Conceptualization, Methodology, Software, Validation**,** Formal analysis, Investigation, Data Curation, Writing - Original Draf, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition

Conflict of Interest Statement

We declare that there is no actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations.

Mariusz Najgebauer, Czestochowa University of Technology
Roman Gozdur, Lodz University of Technology

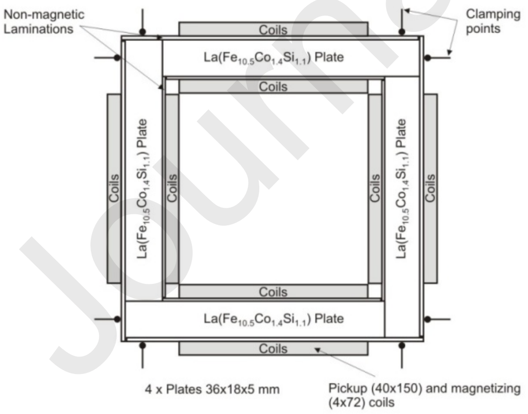


Fig.1. Diagram of assembled magnetocaloric core in the non-magnetic yoke

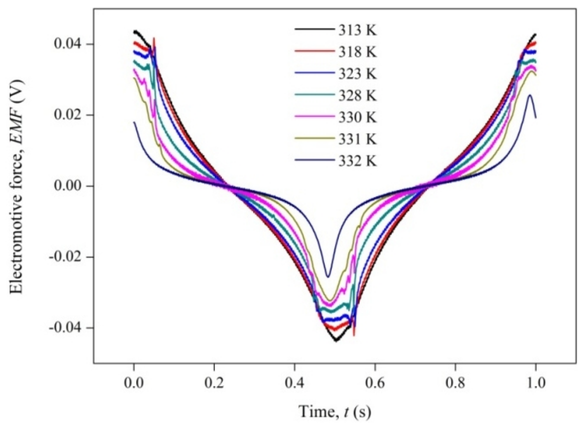


Fig.2.Waveforms of EMF(t) force at different temperatures

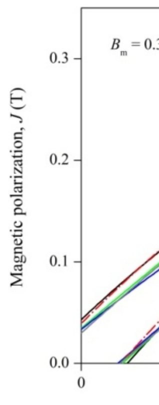


Fig.3. Tempe

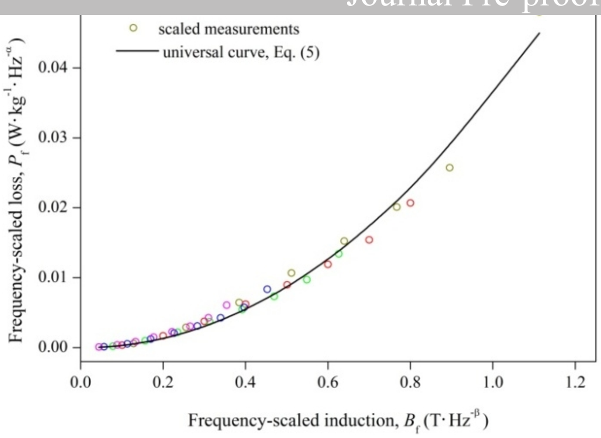


Fig.4. The universal curve of power loss at 315 K

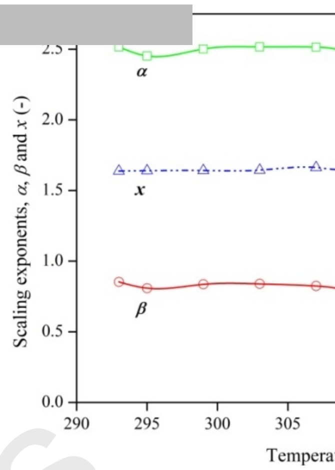


Fig.5. Temperature dependence of t

<u>Highlights</u>

1. The phenomenological, scaling-based method of phase transitions analysis in magnetocaloric alloys was validated.
2. Measured hysteresis loops as well as obtained temperature dependency of the scaling exponents indicated the occurrence of an additional phase transition near the temperature $T = 315$ K
3. This method is an alternative approach to determine the temperature of various phase transitions in magnetocaloric alloys.
4. This method shows high sensitivity, which is manifested by a significant change in the value of scaling parameters in the surrounding of phase transition temperatures. Thereby, it also allows one to determine hardly noticeable phase transitions.