12th Symposium of Magnetic Measurements and Modeling SMMM'2016, Częstochowa–Siewierz, Poland, October 17–19, 2016

Investigation of Critical Behavior in $Gd_{75}Ge_{15}Si_5Ce_5$ Alloy

P. Gębara[a,*] and M. Hasiak[b]

[a]Institute of Physics, Częstochowa Universtity of Technology, al. Armii Krajowej 19, 42-200 Częstochowa, Poland

[b]Department of Mechanics and Materials Science, Wrocław University of Science and Technology, M. Smoluchowskiego 25, 50-370 Wrocław, Poland

The main goal of the present work was to study the critical behavior in the as-quenched $Gd_{75}Ge_{15}Si_5Ce_5$ (wt%) in the vicinity of the critical temperature T_C. The second order phase transition from a ferro- to a paramagnetic state was confirmed by the positive slope of the Arrott plots and analysis of temperature evolution of the Landau coefficients. The critical exponents have been revealed using the Kouvel–Fisher method and yield $\beta = 0.376 \pm 0.006$, $\gamma = 1.032 \pm 0.006$ and $\delta = 3.835 \pm 0.008$. The Curie temperature for the as-quenched $Gd_{75}Ge_{15}Si_5Ce_5$ equals 275.7 ± 0.1 K.

DOI: 10.12693/APhysPolA.131.1232

PACS/topics: 75.30.Sg, 75.50.Bb

1. Introduction

The $Gd_5Si_2Ge_2$ alloy is a well known magnetic material, due to its impressive magnetocaloric properties. In 1997, Pecharsky and Gscheidner Jr. discovered a giant magnetocaloric effect in this alloy [1]. The magnetic entropy change $-\Delta S_M$ calculated for the $Gd_5Si_2Ge_2$ equals 18.5 J/(kg K) under the change of external magnetic field $\Delta(\mu_0 H) = 5$ T at 276 K. Such high value of $|\Delta S_M|$ is caused by two phase transitions (structural and magnetic), which are placed in the same temperature range. Magnetic phase transition is second order at the Curie temperature. Moreover, it is accompanied by structural transformation, which causes a considerable increase of magnetization. For several years, the chemical composition of the $Gd_5Si_2Ge_2$ has been intensively modified in order to improve magnetocaloric properties. As it was shown in [2, 3], the additions such as Al, Cu, Ga, Mn, Co cause an increase in the Curie temperature and imply second order phase transition, which decreases the magnetic entropy change. Hasiak in [4] has shown that small amount of Ni addition leads to decrease of the Curie temperature and slight increase of magnetic entropy change is observed. The investigations of the Gd–Si–Ge alloys concentrate mainly on their magnetocaloric properties. Recently, Franco and co-workers [2] have proposed using the scaling method to reveal critical exponents in Gd–Si–Ge-type alloys. Results obtained by scaling technique compared with critical exponents calculated by Kouvel–Fisher method are in good agreement [5, 6]. As it was shown in [4], the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy exhibits relatively low magnetic entropy change compared to $Gd_{80}Ge_{15}Si_5$. Moreover, the symmetrical shape ΔS_M vs. T curve suggests occurrence of second order phase transition. In this work the detailed study of phase transition observed in the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy has been studied. Additionally, we have investigated values of the critical exponents for the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy.

2. Experimental

The detailed description of sample preparation, structural and magnetic measurements is given in [4]. Phase transition was investigated using the Landau theory. The Curie temperature and values of the critical exponents were studied using the Kouvel–Fisher method.

3. Results and discussion

In order to produce Arrott plots [7], the M vs. $\mu_0 H$ isotherms have been used. Construction of M^2 vs. $\mu_0 H/M$ curves has been done using critical exponents values ($\beta = 0.5$, $\gamma = 1$) related to the mean-field theory. As it is shown in Fig. 1, the M^2 vs. $\mu_0 H/M$ isotherms reveal a positive slope and such behavior suggests a second order phase transition in the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy, according to the Banerjee criterion [8].

The detailed study of phase transition nature near the Curie temperature has been carried out using the Landau theory. Shimizu in [9] showed that magnetic free energy $F(M,T)$ can be expanded in power series of magnetization M in the vicinity of phase transition, according to the following relation:

$$F(M,T) = \frac{c_1(T)}{2}M^2 + \frac{c_2(T)}{4}M^4 + \frac{c_3(T)}{6}M^6 + \ldots - \mu_0 HM, \quad (1)$$

where $F(M,T)$ is magnetic free energy, $c_1(T)$, $c_2(T)$ and $c_3(T)$ are the Landau coefficients, M is magnetization, T is temperature, μ_0 is magnetic permeability of vacuum, H is external magnetic field.

Equilibrium condition $\delta F/\delta M = 0$ makes possible calculation of the Landau coefficients and Eq. (1) can be rewritten in the following form:

$$\mu_0 H = c_1(T)M + c_2(T)M^3 + c_3(T)M^5. \quad (2)$$

Relation (2) was used as a model which was fitted to experimental data. Fitting has revealed values of critical

*corresponding author; e-mail: pgebara@wip.pcz.pl7

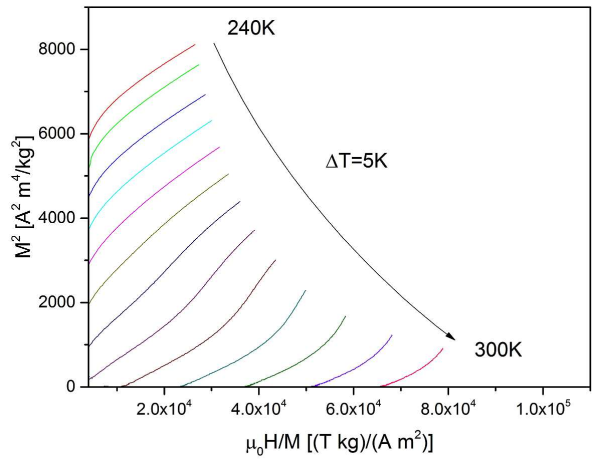

Fig. 1. The Arrott plots constructed for the as-quenched $Gd_{75}Ge_{15}Si_5Ce_5$ alloy using mean field values of critical exponents.

exponents. The $c_1(T)$ and $c_2(T)$ are shown in Fig. 2. The $c_1(T)$ is always positive and has a minimum at the Curie point. The main role in the analysis of phase transition nature plays the sign of c_2 coefficient at the Curie temperature. If the sign of $c_2(T_C)$ is negative the phase transition is of first order. However, if $c_2(T_C)$ value is positive, we observe a second order phase transition. As it is shown in Fig. 2, the value of c_2 coefficient at the Curie temperature is positive and it suggests occurrence second nature of phase transition observed in the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy. Such a result corresponds well with the almost linear shape of the Arrott plots (Fig. 1).

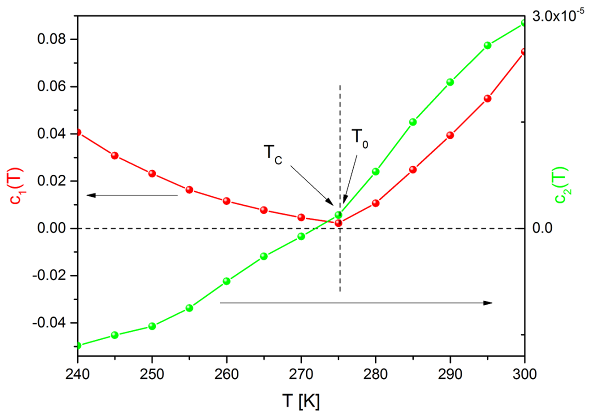

Fig. 2. The temperature dependences of Landau coefficients c_1 and c_2 calculated for the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy.

Second order phase transition in the vicinity of the Curie temperature is described by critical exponents β, γ and δ associated with spontaneous magnetization M_S, initial susceptibility χ_0 and critical magnetization isotherm, respectively. Mathematical relations between these physical quantities and critical exponents are given by [6]:

$$M_S(T) = M_0 \left(-\frac{T - T_C}{T_C}\right)^{\beta}, \ T < T_C, \tag{3}$$

$$\chi_0^{-1}(T) = \frac{H_0}{M_0} \left(\frac{T - T_C}{T_C}\right)^{\gamma}, \ T > T_C, \tag{4}$$

$$M = DH^{1/\delta}, \ T = T_C, \tag{5}$$

where M_S is spontaneous magnetization, H_0, M_0 and D are critical amplitudes.

The part of the Arrott plots, which exhibits nearly parallel lines, has been linearly extrapolated in order to reveal the values of $M_S(T,0)$ and $\chi_0^{-1}(T,0)$. The temperature dependences of M_S and χ_0^{-1} are shown in Fig. 3.

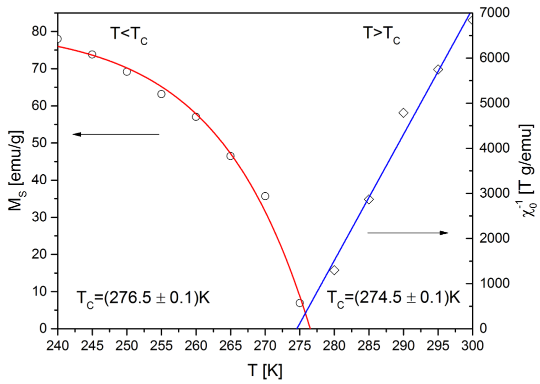

Fig. 3. The temperature dependences of spontaneous magnetization M_S and inverse initial susceptibility χ_0^{-1} of the as-quenched $Gd_{75}Ge_{15}Si_5Ce_5$ alloy.

The M_S and χ_0^{-1} vs. T curves have revealed new, more detailed values of the Curie temperature 276.5 and 274.5 K for $T < T_C$ and $T > T_C$ region, respectively.

The critical exponents can be calculated using the technique proposed by Kouvel and Fisher in [6], which today is known as the Kouvel–Fisher method. According to the Kouvel–Fisher approach, Eqs. (3) and (4) should be rewritten in the following form:

$$M_S(T) \Big/ \frac{\mathrm{d}M_S(T)}{\mathrm{d}T} = \frac{T - T_C}{\beta}, \tag{6}$$

$$\chi_0^{-1}(T) \Big/ \frac{\mathrm{d}\chi_0^{-1}(T)}{\mathrm{d}T} = \frac{T - T_C}{\gamma}. \tag{7}$$

Modification of relations (3) and (4) in the form proposed by Kouvel and Fisher allows their linearization with slopes $1/\beta$ and $1/\gamma$. Linear fitting has revealed values of critical exponents β and γ. Extrapolation of generated linear dependences to the T axis has revealed the Curie points. The Kouvel–Fisher plots are depicted in Fig. 4.

Calculation of critical exponent δ is possible using the Widom scaling relation [10]:

$$\delta = 1 + \gamma/\beta. \tag{8}$$

Basing on exponents β and γ obtained by the Kouvel–Fisher method and relation (8) the value of exponent δ is 3.745.

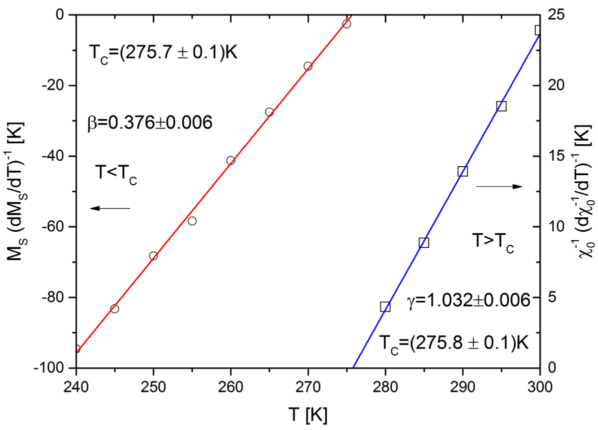

Fig. 4. The Kouvel–Fisher plots for determination β and γ in the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy.

Simple modification of Eq. (5) makes it possible to determine δ. As shown in Fig. 5, the M vs. $\mu_0 H$ curves on a log–log scale collected near T_C are straight lines. The M vs. $\mu_0 H$ isotherms were collected in the temperature range 150–340 K with step 5 K. Due to the fact that the Curie point is about 275.7 K, the field dependence of magnetization measured at 275 K is the closest to T_C. According to that it has been selected as critical isothermal magnetization. The linear fitting with slope a $1/\delta$ has revealed that the δ value is 3.835 ± 0.008. Such a value is in good agreement with δ calculated by the Widom relation.

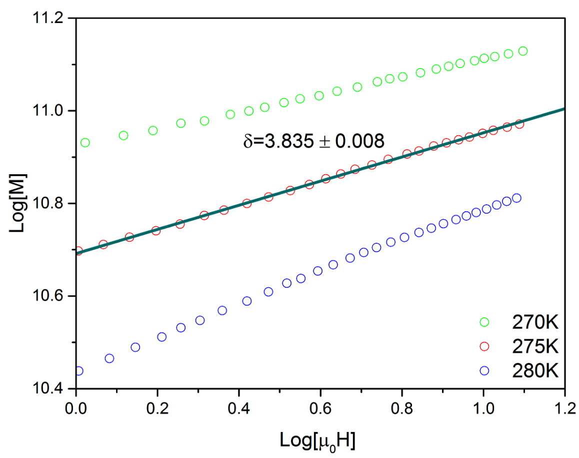

Fig. 5. The M vs. $\mu_0 H$ isotherms on a log–log scale in the vicinity of Curie temperature. The blue line is the linear fit following (5).

The test of revealed exponents is possible using magnetic equation of state [11]:

$$M(H, \varepsilon) = \varepsilon^{\beta} f_{\pm}(H/\varepsilon^{\beta+\gamma}), \qquad (9)$$

where $\varepsilon = (T - T_C)/T_C$, $f_{\pm}$ are regular functions with f_+ and f_- for $T > T_C$ and $T < T_C$, respectively. Equation (9) describes relation $M(H, \varepsilon)\varepsilon^{-\beta}$ vs. $H\varepsilon^{-(\beta+\gamma)}$ and suggests its collapse into two universally different curves, one for temperatures higher than T_C and the other for temperatures lower than T_C. These two universal curves constructed taking into account values of exponents β and γ revealed by the Kouvel–Fisher method are depicted in Fig. 6. The same data on a log–log scale are shown in the inset.

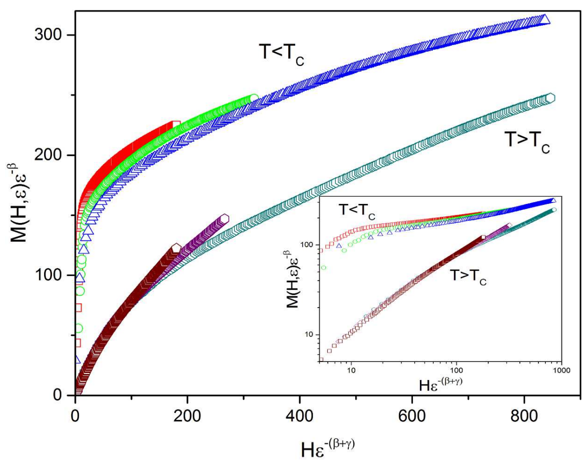

Fig. 6. Scaling plots for the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy. The inset shows the same data on log–log scale.

It is clearly visible that all data collapse on two curves, one for $T > T_C$ and another one for $T < T_C$. Such behavior corroborates that calculated values of critical exponents and the Curie temperature are reasonable and reliable.

The values of critical exponents revealed in this work correspond well with values obtained in [2, 12] for the same group of alloys. Results for critical exponent calculation are collected in Table I together with values corresponding to theoretical models and for a pure Gd.

TABLE I

Critical exponents derived for $Gd_{75}Ge_{15}Si_5Ce_5$ alloy with values delivered by theoretical models and for pure Gd.

	Ref.	β	γ	δ
$Gd_{75}Ge_{15}Si_5Ce_5$ =	this work	0.376	1.032	3.835
$Gd_{4.8}Ce_{0.4}Si_{2.0}Ge_{1.8}$	[Widom]	±0.006	±0.008	3.745
pure Gd	[13]	0.381	1.196	4.139
$Gd_5Si_2Ge_{1.9}Cu_{0.1}$	[2]	0.38	1.15	4.03
$Gd_5Si_2Ge_{1.9}Mn_{0.1}$	[2]	0.41	1.05	3.56
$Gd_5Si_2Ge_{1.9}Ga_{0.1}$	[2]	0.34	1.17	4.44
$Gd_5Si_2Ge_{1.9}Al_{0.1}$	[2]	0.38	1.08	3.84
mean-field	[7]	0.5	1	3
3D-Heisenberg	[7]	0.365	1.386	4.797
3D-Ising	[7]	0.325	1.24	4.82
tricritical mean-field	[14]	0.25	1	5

The γ value corresponds well with the mean-field model. However, values of β and δ are located between values related to the mean-field and 3D-Heisenberg models. Based on these results it is difficult to distinguish, which model describes magnetic behaviors in producing the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy.

4. Conclusions

In present work, the critical behaviors of the $Gd_{75}Ge_{15}Si_5Ce_5$ alloy have been intensively studied in the vicinity of the Curie temperature using the Kouvel–Fisher method and critical isotherm analysis. The reliable and reasonable values of the critical exponents of $\beta = 0.376 \pm 0.006$, $\gamma = 0.032 \pm 0.006$, $\delta = 3.385 \pm 0.008$ and the Curie point 275.7 ± 0.1 K have been calculated. Values of critical exponents have been confirmed by the construction of M–H isotherms, which collapsed into two independent universal branches above and below critical temperature.

References

[1] V.K. Pecharsky, K.A. Gschneidner, *Appl. Phys. Lett.* **70**, 3299 (1997).

[2] V. Franco, A. Conde, V. Provenzano, R.D. Shull, *J. Magn. Magn. Mater.* **322**, 218 (2010).

[3] J. Ferenc, M. Kowalczyk, G. Cieślak, T. Erenc-Sędziak, T. Kulik, *EPJ Web Conf.* **40**, 06005 (2013).

[4] M. Hasiak, *Phys. Status Solidi A* **213**, 1130 (2016).

[5] M.E. Fisher, *Rep. Prog. Phys.* **30**, 615 (1967).

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

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

[8] S.K. Banerjee, *Phys. Lett.* **12**, 16 (1964).

[9] M. Shimizu, *Rep. Prog. Phys.* **44**, 329 (1981).

[10] B. Widom, *J. Chem. Phys.* **43**, 3898 (1965).

[11] H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, London 1971.

[12] Z.R. Zhao, G.F. Wang, X.F. Zhang, *Adv. Mater. Res.* **873**, 855 (2014).

[13] M.N. Deschizeax, G. Delevey, *J. Phys.* **32**, 319 (1971).

[14] D. Kim, B. Revaz, B.L. Zink, F. Hellman, J.J. Rhyne, J.F. Mitchell, *Phys. Rev. Lett.* **89**, 227202 (2002).