Intermetallics 101 (2018) 64–71

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Critical behavior of the ferromagnetic transition in GdSc(Si,Ge) intermetallic compounds

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ARTICLE INFO

Keywords:
GdScSi
GdScGe
Spin-ordering
Thermal properties
Critical behavior
Ferromagnetism

ABSTRACT

A complete study on the critical behavior of the paramagnetic to ferromagnetic transition in intermetallics GdScSi, GdScGe, $GdSc(Si_{0.5}Ge_{0.5})$ and $Gd(Sc_{0.5}Ti_{0.5})Ge$ has been carried out by means of magnetic as well as calorimetric measurements, using a high resolution *ac* photopyroelectric technique. The critical exponents α, β, γ, δ and the ratio of the critical coefficients A^+/A^- have been independently obtained for the four samples. It has been proved that the magnetic interactions are short range as the values of the critical parameters correspond to the 3D-Heisenberg class, stating an isotropic ordering of the Gd spins. In some cases, there are small deviations of some of the critical parameters from the theoretical values which have been discussed on the basis of the variation of the *d* states hybridization between the rare earth and the transition metal, as well as the presence of small magnetocrystalline anisotropies arising from spin-orbit coupling effects.

1. Introduction

Ternary intermetallic systems *R-T-X* (*R* = rare earth, *T* = transition metal, *X* = *p*-block element) are being extensively studied as promising magnetic systems for technological applications, specially due to the high temperature of their magnetic transitions. This makes them suitable candidates to look into the possibility of presenting strong magnetocaloric effects [1]. To this end, a knowledge as broad as possible of their properties (crystallographic as well as magnetic) is desirable. In particular, some extensive studies have already been undertaken on *R*ScSi, *R*ScGe, *R*TiSi, *R*TiGe (*R* = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Y) [2–14]; however, there is an aspect which has been seldom studied up to now, and this is the critical behavior of the magnetic transitions, which gives valuable information about the range and dimensionality of the magnetic exchange interactions, together with the role that other mechanisms can play if the critical parameters obtained do not match a particular universality class. The knowledge of the variations of the universality class (which is tantamount to the physical mechanisms involved) with *R*, with *T* or with *X* (even with admixtures of *T*, *X*) will have to be taken into account when designing compositions in search of a strong magnetocaloric material.

Scaling analysis within the framework of renormalization group theory has established that the critical behavior of second order phase transitions in the near vicinity of the critical temperature T_C is characterized by a set of critical exponents α, β, γ, δ … associated with different thermal and magnetic properties, with interrelated values [15]. Each set of exponents (grouped in universality classes) is the result of proposing a different Hamiltonian to describe the physical system. For ferromagnetic materials, the most common universality classes with the corresponding values of the critical exponents are shown in Table 1 [16–19]. If long-range interactions are at the core of the magnetic interactions, the mean-field model should be the right one. The other three classes involve short-range order interactions: the Heisenberg model corresponds to an isotropic ferromagnetic material, XY model implies an easy-plane ferromagnetism while the Ising model is related to uniaxial anisotropy of the spins.

The critical exponent α is associated to the specific heat,

$$c_p(T) \sim A^{\pm} |t|^{-\alpha} (A^- \text{ for } T < T_C, A^+ \text{ for } T > T_C) \quad (1)$$

As a function of the reduced temperature $t = (T-T_C)/T_C$; this equation holds in the close vicinity of the critical temperature. On the other hand, β, γ and δ are associated with magnetic variables: the spontaneous magnetization (M_S), the inverse of initial susceptibility (χ_0^{-1}) and the critical isotherm, respectively:

$$M_S(T) \sim |t|^{\beta} \; (T < T_C), \quad (2)$$

$$\chi_0^{-1}(T) \sim |t|^{\gamma} \; (T > T_C), \quad (3)$$

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https://doi.org/10.1016/j.intermet.2018.07.011
Received 10 May 2018; Received in revised form 3 July 2018; Accepted 21 July 2018

Table 1
Main universality classes for different magnetic systems [15–19].

Universality class	α	β	γ	δ	A^+/A^-
Mean-field Model	0	0.5	1.0	3.0	–
3D-Ising	0.11	0.3265	1.237	4.79	0.53
3D-XY	−0.014	0.34	1.30	4.82	1.06
3D-Heisenberg	−0.134	0.365	1.386	4.80	1.52

$$M(H) \sim H^{1/\delta}\ (T = T_C). \tag{4}$$

The critical exponents are also involved in the magnetic equation of state in the critical region, which is given by

$$M\ (H,\ t) = |t|^{\beta} f_{\pm}\ (H/|t|^{\beta+\gamma}) \tag{5}$$

Where f_- and f_+ are regular analytic functions for $T < T_C$ and $T > T_C$, respectively.

In this study we are focusing our attention on some Gd members of this family, as they have the highest Curie temperature, slightly above room temperature, which make them good candidates for technological applications. We are presenting a complete study of the critical exponents (α, β, γ and δ) for the GdScSi, GdScGe, GdSc($Si_{0.5}Ge_{0.5}$), Gd($Sc_{0.5}Ti_{0.5}$)Ge compounds, in order to acknowledge whether, and how, a change in either the *p*-block element or the transition metal can alter their critical behavior.

2. Materials and methods

Small samples of the ternary and pseudo-ternary compounds Gd(Sc,Ti)(Si,Ge), in form of polycrystalline alloys, were prepared and utilized in this work. The starting materials were high purity elements supplied by commercial vendors: 99.9 wt.% for both Gd and Sc (*R* metals from Koch-Light, England), 99.99 + wt.% Ti (from Aldrich Chem. USA), and 99.9999 wt.% for Si and Ge (from Alfa-Aesar, Germany). The alloys were prepared by arc melting stoichiometric amounts of the elements under a pure argon atmosphere on a water-cooled copper hearth; after a first melting and reaction of elements, the buttons were re-melted four times (turning them upside-down each time) to ensure homogenization (total weight of about 2 g; weight loss lower than 0.2 wt.%). The final alloys were placed inside an outgassed Ta tube, sealed under vacuum in silica tubes and annealed at 1000 °C for 10 days. Phase analysis, to check for quality of the samples was performed by X-ray powder diffraction using a Guinier camera [Cu Kα1 radiation; Si as internal standard (a = 5.4308(1) Å] and optical microscopy. Indexing of the powder diffraction patterns was carried out by comparison with the pattern calculated by the help of the Lazy-Pulverix program [20]; then, the lattice parameters calculated by least-squares fit. The alloys, prepared as above, resulted to be practically single phase: in the two samples containing Si only a 2–3 vol% of $Gd_{5-x}Sc_xSi_3$ (Mn_5Si_3-type) was present as secondary phase, while in the other two containing Ge the homologous phase $Gd_{5-x}Sc_xGe_3$ [21] was not even detectable (from Guinier pattern and as grain separation in the micrographic specimens).

Magnetization (*M*) measurements have been carried out in a VSM (Vibrating Sample Magnetometer) by Cryogenic Limited under external applied magnetic fields H_a ranging from 0 to 80 kOe. In order to completely cover the critical region, isotherms have been collected over a range of about ± 30 K around T_C (ΔT = 1 K). The applied magnetic field H_a has been corrected for demagnetization effects and the internal field calculated using the relation $H_i = H_a - NM$, where M is the measured magnetization and N the demagnetization factor. This demagnetization factor has been obtained using the method given in Refs. [22,23], measuring the zero-field ac susceptibility. The so obtained H_i has been the one used for the scaling analysis. The magnetic susceptibility was measured with AC Measurement System Option in PPMS (Physical Properties Measurement System) by Quantum Design.

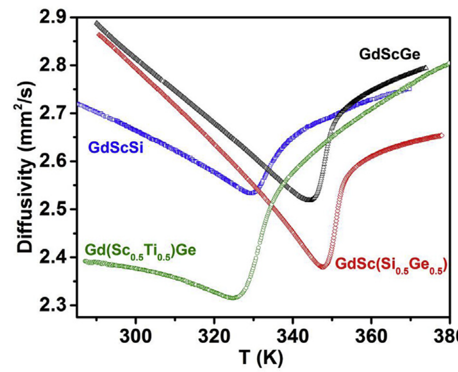

Fig. 1. Thermal diffusivity as a function of temperature for GdScSi (■), GdScGe (▲), GdSc(Si0.5Ge0.5) (◆), Gs(Sc0.5Ti0.5)Ge (●). Not all points are shown, for the sake of clarity.

A high resolution *ac* photopyroelectric calorimeter in the back detection configuration has been used for the thermal measurements. Both thermal diffusivity and specific heat have been obtained for each of the four samples as a function of temperature in the region around the Curie temperature. This technique is very well suited to study the critical behavior in phase transitions and has been successfully applied to liquid crystals and solids (magnetic as well as ferroelectric transitions), including other intermetallic families [24–32]. The details of the experimental setup, as well as of the theory explaining how to retrieve the thermal variables from the photopyroelectric signal, can be found elsewhere [24,33].

3. Experimental results and data fittings

The thermal diffusivity as a function of temperature for the four samples is shown in Fig. 1, from room temperature up to approximately 380 K. In all cases, the ferromagnetic phase transition is marked as a dip which alters the monotonic decrease from high temperatures to lower ones which is characteristic of intermetallic materials when there is no phase transition [34,35]. In other members of the same intermetallic family (NdScSi, NdScGe) with ferromagnetic transitions, the same behavior and dip have been observed [32]. This kind of dip signaling a ferromagnetic transition is common in many other magnetic materials, such as manganites [36,37] but with the difference that in the latter, as thermal insulators, the thermal diffusivity monotonically increases while temperature is reduced. Starting from GdScGe, which has the higher values of thermal diffusivity, the substitution of Ge by 50% Si reduces somewhat the thermal diffusivity and slightly shifts the critical temperature to higher temperature while the shape of the dip is very similar. The total substitution of Ge by Si, on the other hand, shifts down the critical temperature about 15 K and makes the dip shallower, with a thermal diffusivity in general smaller than the one for GdScGe. Finally, the substitution of 50% Sc by Ti does introduce a big change in the general shape of the curve, reducing even more the thermal diffusivities values while shifting down the Curie temperature about 15 K.

Fig. 2 shows the magnetization per unit mass as a function of temperature for the four samples. All of them are very similar in shape, with the non-codoped samples GeScSi and GeScGe giving the higher values.

In what follows we are going to present the scaling analysis of the four samples, in parallel. In the text and in the figures, *H* will mean the internal field H_i, to simplify the notation. The usual procedure is, first, to represent the standard Arrott Plot (M^2 as a function of H/M) for isotherms in an appropriate temperature range around the Curie temperature in each case (301–356 K for GdScSi, 316–374 K for GdScGe, 318–372 K for GdSc($Si_{0.5}Ge_{0.5}$) and 301–360 K for Gd($Sc_{0.5}Ti_{0.5}$)Ge. If long-range interactions were responsible for the ferromagnetic transition, there would be a linear behavior at high fields on that plot. Fig. 3a