PAPER

Observation of short range ferromagnetic interactions and magnetocaloric effect in cobalt substituted Gd₅Si₂Ge₂

Bhagya Uthaman, A P. Manju, b Senoy Thomas, a Deepshikha Jaiswal Nagar, b K. G. Suresh c and Manoj Raama Varma d

We report on the observation of double transition – a first order and a second order transition in Gd₅Si₂₋ₓCoₓGe₂ with x = 0, 0.1, 0.2 and 0.4 with the appearance of short-range ferromagnetic correlations. The first order phase transition is due to a combined magnetostructural transition from monoclinic paramagnetic phase to orthorhombic ferromagnetic phase on cooling while the second order transition arises from an orthorhombic paramagnetic to ferromagnetic phase on cooling. Structural studies show that the substituted compounds crystallize in a combination of Gd₅Si₂Ge₂ and Gd₅Si₄ phases. Low-temperature X-ray diffraction measurements confirm the complete transformation from monoclinic to orthorhombic phase. DC magnetization measurements reveal an anomalous low field magnetic behaviour indicating a Griffiths-like phase. This unusual behaviour is attributed to the local disorder within the crystallographic structure indicating the presence of short-range magnetic correlations and ferromagnetic clustering, which is stabilized and enhanced by competing intra-layer and inter-layer magnetic interactions. The magnetostructural transition results in entropy changes (ΔSₐ) of 9 J kg⁻¹ K⁻¹ at 260 K for x = 0, 8.5 J kg⁻¹ K⁻¹ at 245 K for x = 0.2 and 4.2 J kg⁻¹ K⁻¹ at 210 K for x = 0.4 for a field change of 50 kOe. Co substitution induces compelling crystallographic and magnetoresponsive effects in the Gd₅Si₂Ge₂ system, which could be useful for potential and smart applications such as solid-state magnetic refrigeration and sensitive magnetic switching from paramagnetic to ferromagnetic state. Universal curve analysis has been carried out on the substituted samples to study the order of the magnetic transition.

I. Introduction

The Gd₅(Si₂Ge₁₋ₓ)₄ intermetallic compounds constitute an interesting class of compounds exhibiting multifunctional properties such as giant magnetocaloric effect (GMCE), colossal magnetostriction, giant magneto-resistance, and spontaneous generation of voltage. The unusually strong magneto-responsive properties in this system are attributed to the first-order magnetostructural transition from a high-temperature monoclinic (M) paramagnetic (PM) phase to a low-temperature orthorhombic (O(i)) ferromagnetic (FM) phase in the vicinity of the magnetic ordering temperature. The phase transition in these compounds can be triggered reversibly by temperature, magnetic field, hydrostatic pressure as well as by tuning the Si:Ge ratio. Magnetic refrigeration, a potential cooling technology based on magnetocaloric effect (MCE), has initiated intensive research activity in the recent years owing to its high cooling efficiency and eco-friendly nature. Currently, it is pursued as the most efficient, easily accessible, and highly economical cooling technology compared to the existing vapor compression-expansion based refrigeration technology. MCE is a thermodynamic phenomenon which enables the refrigerant temperature to change with applied magnetic fields and is manifested as the reversible heating or cooling of a magnetic material upon the application of a field. The adiabatic magnetization of the material causes the entropy of the spin subsystem to decrease, leading to the heating of the material, and when this magnetic field is removed adiabatically, the material gets cooled. Various magnetocaloric material classes such as manganites, intermetallics, etc. and their properties have been discussed in recent years throwing light on the development of energy efficient materials for solid state cooling.

Magnetic refrigerants, such as Gd–Si–Ge, La–Fe–Si and its hydrides, Mn–Fe–P–As and Ni–Mn–Z (Z = In, Sn, Sb, Ga) based Heusler alloys have come to research focus due to

---

a Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram-695 019, India. E-mail: manoj@niist.res.in, manojraamavarma@yahoo.co.uk
b Indian Institute of Science Education and Research, Thiruvananthapuram-695 016, India
c Department of Physics, Indian Institute of Technology, Mumbai-400076, India
d Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cp00849j
their giant MCE caused by the first-order phase transition (FOPT). Efforts are being made to find alternative technologies to replace the conventional gas compression–expansion technique for cooling applications. Besides its practical application as a magnetic refrigerant, MCE studies can give an extra insight into the properties of the magnetic phase transitions. From the point of application, it is crucial that a magnetic refrigerant material possesses a large magnetic entropy change ($\Delta S_m$) in addition to a large refrigeration capacity (RC).

The remarkable properties of Gd$_x$(Si$_x$Ge$_{1-x}$)$_4$ family is associated with its unique, intrinsically layered crystal structure built by the stacking of stable two-dimensional subnanometer-thick slabs of Gd and Si/Ge atoms. The crystallographic phase and the nature of the magnetic interactions are controlled by a number of interlayer covalent like Si(Ge)–Si(Ge) bonds connecting the slabs.6,12–14 The martensitic-like collective shear movement of these slabs via changing specific Si(Ge)–Si(Ge) bonds gives rise to different crystal structures in this family of materials. When all the slabs are connected through strong Si(Ge)–Si(Ge) bonds, the compounds adopt the O(i) Gd$_5$Si$_4$ structure with Pnma space group, whereas those without any inter-slab Si(Ge)–Si(Ge) bonding possess the orthorhombic O(n) Sm$_2$Ge$_4$ structure with Pnma space group. When the alternate slabs are connected through Si(Ge)–Si(Ge) bonds, the compounds crystallize in monoclinic Gd$_5$Si$_4$Ge$_2$ structure with space group P112$_1$/a.6,32–36 The presence of Griffiths-like phases (GP) in several compounds of the R$_x$(Si$_x$Ge$_{1-x}$)$_4$ family (R = Gd, Tb, Dy and Ho) adopting the M and O(n) structural phases at room temperature have also attracted much attention recently.37–39 The appearance of GP arises from the local disorder within the crystallographic lattice which is stabilized and enhanced by the competing inter-layer and intra-layer magnetic interactions.37–39

It has been reported that the addition of small amounts of 3d elements (Fe, Co, Ni, or Cu) and p elements (Al, C) (0.33 at. wt%) for Si and Ge in the Gd$_5$Si$_2$Ge$_2$ alloy increase the Curie temperature ($T_C$) but have an adverse effect on the magnetocaloric properties.40 Zhang et al. reported a considerable reduction in thermal hysteresis with the addition of transition elements (Fe, Co, Mn and Ni).41 Provenzano et al. reported the reduction in hysteresis losses with the substitution of Fe.42 Shull et al. found that the addition of Cu, Co, Ga, Mn and Al (0.1 at. wt%) at the Ge site completely eliminated the hysteresis loss, broadened the magnetic entropy change and shifted its peak position from 275 K to 305 K. However, doping the same amount of either Sn or Bi had a negligible effect on the magnetocaloric properties.43 Podmiljšak et al. found that the substitution of Fe at the Si site results in the decrease of $T_C$ and MCE while Fe substitution at the Ge site would result in an increase of $T_C$ but with a reduced MCE.44 The reduction in magnetic entropy change with Fe substitution in Gd$_5$Si$_4$Ge$_2$ and Gd$_5$Si$_4$Ge$_{1.8-}$Fe$_{0.2}$ alloys was reported by Raj Kumar et al.45,46

In this paper, we report the observation of short-range ferromagnetic correlations within the PM matrix, in cobalt substituted Gd$_5$Si$_4$Ge$_2$. The substitution of Co at the Si site has a strong influence on the structure and magnetic properties of Gd$_5$Si$_4$Ge$_2$ which is attributed to the stabilization of the O(i) component. The effect of Co substitution on the magnetocaloric behaviour of Gd$_5$Si$_4$Ge$_2$ is also investigated and the universal scaling analysis based on magnetic entropy change is also applied to understand the nature of magnetic transition.

II. Experimental

Polycrystalline ingots of Gd$_5$Si$_{1-x}$Co$_x$Ge$_2$ with $x = 0, 0.1, 0.2$ and 0.4 were prepared by arc melting the constituent elements in a water cooled copper hearth in high purity argon atmosphere. The purity of the starting elements was 99.99 wt% for Gd and 99.9999 wt% for Ge, Si and Co. The ingots were turned over after each melting and remelted four times to ensure compositional homogeneity during melting. Weight loss of the samples after the arc-melting process was found to be less than 0.01%. As-cast ingots were sealed in evacuated quartz tubes and annealed at 1573 K for 1 hour and subsequently quenched in ice water. The crystal structure of the samples were analyzed by X-ray powder diffraction using PANalytical X’pert Pro diffractometer with Cu-K$_{\alpha}$ radiation operated at 40 kV and 30 mA at room temperature. The diffraction measurements were performed in the 2$\theta$ range 20° to 60° with a step size of 0.017°. Rietveld refinement of the diffraction pattern was carried out using GSAS (General Structure Analysis System)-EXPGUI software.47 The low temperature powder X-ray diffraction measurements were done on an Oxford Cryosystems closed cycle helium cryostat (Model: Phenix) mounted on a vertical goniometer in a PANalytical Empyrean powder X-ray diffractometer with CuK$_{\alpha}$ and CuK$_{\beta}$ radiations for 1 hour in the 2$\theta$ range 5° to 80° with a step size of 0.017°. The microstructural features were seen under Back-scattered secondary electron (BSE) imaging mode by using scanning electron microscope (SEM) of Carl Zeiss Evo 18 equipped with an energy dispersive X-ray spectroscopy (EDS) system (Oxford EDAX X-Max$^+$). Qualitative analysis was carried out by EDS to know the chemical composition of these alloys. Differential scanning calorimetry was performed (PerkinElmer-Pyris 6) with a scanning rate of 5° C min$^{-1}$ under nitrogen atmosphere. Electron spin resonance (ESR) measurements were obtained using JES – FA200 ESR Spectrometer (ESR-JEOL, Japan) at selected temperatures between 200 K and 320 K. Magnetization measurements were made as a function of both temperature and field using a Physical Property Measurement System [Quantum Design, Dynacool] up to a maximum field ($H$) of 50 kOe in a temperature range 100–320 K. MCE was estimated, in terms of isothermal magnetic entropy change ($\Delta S_m$), from Maxwell relations.11,14

III. Results and discussion

A. Structural analysis

Fig. 1 shows the X-ray diffraction patterns (XRD) at room temperature of Gd$_5$Si$_{1-x}$Co$_x$Ge$_2$ with $x = 0, 0.1, 0.2$ and 0.4. All the compositions crystallize in a mixed state of monoclinic (M) Gd$_5$Si$_4$Ge$_2$ phase and orthorhombic (O(i)) Gd$_5$Si$_4$ phase at room temperature. The monoclinic Gd$_5$Si$_4$Ge$_2$ phase has been
indexed with ICSD pattern no. 84084 (space group \(P11_2_1/a\)) while the O(i) \(Gd_5Si_4\) structure has been indexed with ICSD pattern no. 84083 (space group \(Pnma\)). A small fraction of hexagonal \(Gd_5Si_3\) secondary phase is also present in our samples and has been indexed with ICSD pattern no. 99641 (space group \(P6_3/mcm\)). Rietveld refinement results shown in Fig. 2 confirms the presence of monoclinic, O(i) and hexagonal phases in \(Gd_5Si_2Co_xGe_2\) with \(x = 0, 0.1, 0.2\) and 0.4. The lattice parameters extracted along with refinement parameters are summarized in Table 1. The presence of the secondary \(Gd_5Si_3\) phase has been confirmed from SEM and EDS analysis of the samples and more details are discussed in the next section.

Fig. 3 shows the XRD patterns of \(Gd_5Si_{1.9}Co_{0.1}Ge_2\) compound at various temperatures in between 200 K and 300 K. At room temperature, the alloys exists in a combination of monoclinic, O(i) and hexagonal phases. As the temperature is decreased from 300 K, it can be seen that O(i) phase starts dominating in the system. This is evident at 255 K. The appearance of the peak corresponding to (230) at 30° at 255 K shows the presence of O(i) phase while the complete disappearance of the peak corresponding to (2–31) at 240 K shows the complete structural transformation of mixed M + O(i) phase to a single O(i) phase. The refined XRD patterns for 300 K and 200 K are shown in Fig. S1 (see ESI†) and the parameters extracted from the refinement are tabulated in Table S1 (see ESI†).

**B. SEM and TEM analysis**

The backscattered scanning electron (BSE) micrographs of cobalt substituted \(Gd_5Si_2Ge_2\) alloys is shown in Fig. 4. The microstructures of the cobalt containing alloys display a multi-phase nature showing the presence of a brighter \(Gd_5(Si,Ge)_4\) matrix phase (3:4-type with M + O(i) phases) along with darker \(Gd_5(Si,Ge)_3\) (5:3-type) secondary phase. Elemental mapping analysis has been performed on all the samples and the results of \(x = 0.1\) are included in Fig. 4 as a representative of the series. The BSE micrographs and elemental mapping of \(x = 0.2\) and \(x = 0.4\) are shown in Fig S2 and S3 (see ESI†) respectively. The EDS spectra of the matrix phase and darker grain boundary region for \(x = 0.1\) is shown in Fig. S4 (see ESI†). Elemental mapping reveals that cobalt is completely absent in the matrix phase but segregated into the grain boundary. The grain boundary phase is enriched with Si and Co as can be seen from Fig. 4. The complete absence of Co in the dominant matrix phase 5:4, suggests that cobalt does not dissolve in the matrix but is primarily accumulated in the secondary 5:3 phase. A similar result has been observed for Fe substitution in \(Gd_5(Si_{0.6}Ge_{0.4})_4\)\(^{42,45,46}\) and \(Tb_5Si_2Ge_2\)\(^{48}\) wherein the substituted iron does not dissolve in the matrix but combines with silicon forming secondary phases. These results suggest that upon cobalt addition, it primarily combines with the silicon giving rise to a grain boundary phase enriched with silicon and cobalt. The EDS results are summarized in Table 2. Moreover, the EDS results indicate that the 5:4 phase contains a greater concentration of
Ge which results in the increase of lattice volume of the matrix phase (M + O(I)) with increase in Co substitution. This is concordant with our Rietveld refinement results shown in Table 1. From the SEM images, it is quite difficult to distinguish the presence of monoclinic and O(I) phases. Hence, to have a better understanding of the different matrix phases, we have carried out the High-Resolution Transmission electron microscopy (HRTEM) analysis on the substituted samples Gd$_5$Si$_2$Co$_x$Ge$_2$ with $x = 0.1$, 0.2 and 0.4 and the results are depicted in Fig. 5.

The dominant planes seen in the high-resolution bright field images matches with the planes of the monoclinic and O(I) phase. Interplanar spacing ($d$) of these planes measured from the TEM images match with the calculated values of the corresponding planes. The selected area electron diffraction (SAED) patterns recorded shows a spotty nature. The $d$ values corresponding to these spots and the corresponding SAED patterns are indexed as shown in Fig. 5.
C. DSC measurements

Fig. 6 shows the DSC curves of Gd$_5$Si$_2$Ge$_2$ with $x = 0.1$, 0.2 and 0.4 during heating and cooling cycles. During heating, all the compounds show an endothermic dip, and an exothermic peak on cooling. The dips at 259 K, 248 K and 227 K for $x = 0.1$, 0.2 and 0.4 during heating is attributed to a first order phase transition from an O(I) phase to a monoclinic phase. Furthermore, it can be noted that the phase transformation is completely reversible during the following cooling cycle. XRD, together with DSC results, indicate that Gd$_5$Si$_2$Ge$_2$ samples with $x = 0.1$, 0.2 and 0.4 undergoes a first-order structural phase transition on temperature change. The transition temperatures decrease with an increase in Co content up to $x = 0.4$.

D. Magnetic characterization

Fig. 7 shows the temperature dependent magnetization ($M$–$T$) data taken in the Field-Cooled-Cool (FCC) and Field-Cooled-Warm (FCW) modes in an applied field of 500 Oe for $x = 0.1$, 0.2 and 0.4. Two transitions are observed in the magnetization data for both the samples. For $x = 0.1$, the first one at 292 K indicates a second order phase transition from O(I) FM phase to O(I)PM phase on heating. The second transition occurs at 255 K and it is a first order transition from O(I) FM phase to monoclinic PM phase as is evident from the hysteresis between the FCC and FCW data on heating. Similarly, for $x = 0.2$, the first transition at 291 K corresponds to a second order magnetic phase transition while the second transition at 240 K is a first-order structural phase transition. The $M$–$T$ results are concordant with our XRD results showing the presence of two phases coexisting in the system at room temperature giving rise to two sets of phase transitions in the system.

$M$–$T$ measurements have also been carried out in the substituted samples at different fields of 100 Oe, 500 Oe, 1000 Oe, 5000 Oe and 10 000 Oe and are shown in Fig. 8(a)–(c). The smearing out of phase transitions at higher magnetic fields is clearly visible which is due to the masking of the FM signal by the rising PM background. Fig. 8(d)–(f) shows the inverse susceptibility ($\chi^{-1}$) at different fields of 100 Oe, 500 Oe, 1000 Oe, 5000 Oe and 10 000 Oe. At higher temperatures, the linear behaviour of $\chi^{-1}$ with temperature indicates that $\chi^{-1}$ obeys the Curie–Weiss (CW) law, $M/H = C/(T - \theta)$. At large applied magnetic fields, the FM component is suppressed in the PM

<table>
<thead>
<tr>
<th>$x$</th>
<th>Phase</th>
<th>Gd</th>
<th>Si</th>
<th>Ge</th>
<th>Co</th>
<th>Phase type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Matrix</td>
<td>55.13</td>
<td>20.53</td>
<td>24.34</td>
<td>—</td>
<td>5:4</td>
</tr>
<tr>
<td></td>
<td>Grain boundary phase</td>
<td>62.06</td>
<td>21.24</td>
<td>15.74</td>
<td>0.96</td>
<td>5:3</td>
</tr>
<tr>
<td>0.2</td>
<td>Matrix</td>
<td>55.48</td>
<td>20.5</td>
<td>24.02</td>
<td>—</td>
<td>5:4</td>
</tr>
<tr>
<td></td>
<td>Grain boundary phase</td>
<td>62.53</td>
<td>20.98</td>
<td>14.48</td>
<td>2.01</td>
<td>5:3</td>
</tr>
<tr>
<td>0.4</td>
<td>Matrix</td>
<td>55.93</td>
<td>20.36</td>
<td>23.71</td>
<td>—</td>
<td>5:4</td>
</tr>
<tr>
<td></td>
<td>Grain boundary phase</td>
<td>62.87</td>
<td>19.96</td>
<td>13.39</td>
<td>3.78</td>
<td>5:3</td>
</tr>
</tbody>
</table>
matrix, and the CW law is obeyed throughout the PM region and yields a PM Weiss temperature, \( \theta_P \) of 260 K, 264 K, 234 K respectively for \( x = 0.1, 0.2 \) and 0.4. The positive value of \( \theta_P \) indicates that FM interactions are dominant in this compound. A clear deviation from CW behaviour is observed for a small applied magnetic field below a particular temperature. This is similar to the previous observations in Griffiths like phases.\(^{37–39}\)

The temperature of deviation is denoted as the Griffiths temperature \( T_G \), and is shown in Fig. 8(d)–(f). The downturn below \( T_G \) is a signature of GP, a unique feature exhibited by magnetic materials which show a strong correlation between structural and magnetic properties. This is usually reflected as a downturn in \( \chi^{-1} \) as a function of temperature above \( T_C \). On increasing the magnetic field, the anomaly in \( \chi^{-1} \) is suppressed and becomes nearly indistinguishable from the values at high temperature. It can be seen that with an increase in Co concentration to 0.4, the GP are not suppressed even at 10000 Oe, suggesting that higher fields are necessary for their complete suppression.

In the original model, Griffiths considered the percolative nature of a random Ising ferromagnet having nearest neighbor exchange interaction with strength \( J \) and 0 distributed randomly with probability \( p \) and \( 1 - p \), respectively. That is, above the ferromagnetic transition point in a disordered system, there is always a finite probability of finding an arbitrary large ferromagnetic cluster. For \( p < p_c \), there is no long-range FM order. Here \( p_c \) is the precolative threshold. Above \( p_c \), the FM phase exists in a weakened form by the shortage of percolation path and hence, thermal fluctuations will destroy the FM phase at a temperature \( T_C \), which is lower than the magnetic ordering temperature \( (T_M) \) of the undiluted/pure FM system. The region, \( T_C < T < T_G \), where the system is characterized by the coexistence of FM clusters within the PM matrix, is referred to as the Griffiths phase regime. In this temperature regime, \( \chi^{-1} \) could deviate from its expected Curie–Weiss linear behaviour. This deviation starts, exactly at \( T_G \), on cooling the diluted system, as if the system somehow recalled that its magnetic ordering temperature was \( T_G \) before it became diluted.\(^{51–53}\) The basic characteristic of the GP regime \( (T_C < T < T_G) \) is that in this regime due to the absence of long-range FM order, the spontaneous magnetization is zero.\(^{54}\)

In the classical Griffiths model, the exchange bonds are broken randomly but, being broken, they remain fixed relative to the crystallographic lattice. Similar observations have been made in substituted manganites. In the case of substituted manganites, GP arises mainly due to two reasons: size mismatch and due to the change in the nature of the double exchange interaction between Mn\(^{3+}\)–Mn\(^{4+}\) due to the introduction of new cations at the A site. For example, in La\(_{1-x}\)B\(_x\)MnO\(_3\) where B = Ca, Sr, Ba,\(^{50,55,56}\) the source of the disorder is the random substitution of La\(^{3+}\) by ions with different sizes and valence states. The probability \( p \), for the existence of a FM bond increases with \( x \),

---

**Fig. 7**  \( M-T \) curves of Gd\(_x\)Si\(_2-y\)Co\(_y\)Ge\(_2\) with \( x = 0, 0.1, 0.2 \) and 0.4 alloys measured in a magnetic field of 500 Oe during FCC and FCW processes. Inset depicts \( \text{d}M/\text{d}T \) as a function of temperature showing transition temperatures.
because the increasing number of Mn$^{3+}$–Mn$^{4+}$ pairs enhances the double-exchange (DE) driven FM interaction. Because of the static Jahn–Teller (JT) distortion of the Mn$^{3+}$ ions, the non-JT active Mn$^{4+}$ ions and the FM bonds can be regarded as fixed within the lattice resulting in quenched disorder, which results in the development of the GP.\cite{55,57,58} In (La$_{1-x}$Pr$_x$)$_{0.7}$Ca$_{0.3}$Mn$_{16/18}$O$_{39}$, the phase competition between the FM-antiferromagnetic (AFM) phase results in the nucleation of the GP.

In R$_5$(Si$_{x}$Ge$_{1-x}$)$_2$ (R = rare earth), the appearance of this regime is attributed to the strong interplay between structure and magnetism present in these materials. Their complex nanostructured crystalline structure is formed by the stacking of rigid two dimensional slabs of R and T = Si/Ge. At the interface between these two building blocks, the formation/rupture of Si(Ge)–Si(Ge) dimers linked through covalent bonds occur. The actual crystallographic phase and nature of the magnetic interactions are controlled by the number of inter-layer covalent-like T–T bonds connecting the slabs, which results in the development of two different magnetic interactions in the system. The intra-slab magnetic exchange interaction, $J_{\text{intra}}$ is ruled by the conventional 4f–4f Ruderman–Kittel–Kasuya–Yosida (RKKY)
indirect exchange, and the inter-slab magnetic interactions $J_{\text{inter}}$ are influenced by an additional R–T–T–R superexchange interaction via the existing T–T bonds.\(^{24}\) The intra-layer magnetic structure is essentially FM. On the other hand, depending on the number of inter-slab pairs which are covalently bonded,\(^{36}\) the inter-layer coupling tends to be either FM or AFM. Hence, in $R_5(Si_{1-x}Ge_x)_3$ compounds, GP originates from the local disorder within the crystallographic lattice, which is stabilized and enhanced by the competing inter-layer and intra-layer magnetic interactions. The disorder is linked to the percolation mechanism where, Ge substitution for Si results in the breakdown of FM order. When Ge is absent, or its concentration is such that $x > x_p$ ($x_p$ is defined as the critical Si concentration), the system stabilizes in the O(I) structure where all the inter-slab bonds are formed and the system has a FM character. At $x = x_p$, the Ge atoms start substituting Si atoms at the inter-slab sites, i.e., the system becomes more diluted. This promotes an increase in the distance between consecutive slabs due to the higher atomic radius of Ge and the inter-slab covalent bonds begin to break leading to the destruction of the FM order and a decrease of the magnetic exchange energy resulting in a decrease in $T_C$. When a critical Ge concentration limit is reached ($x_c$), the RKKY interaction becomes negative and consequently, the antiferromagnetic state becomes the most stable one as beyond $x_c$, it is not possible to achieve long-range FM order. The existence of the two competing interactions $J_{\text{intra}}$ and $J_{\text{inter}}$ leads to the enhancement of the FM short-range correlations. Hence, it can be stated that in $R_5(Si_{1-x}Ge_x)_3$ compounds exhibiting GP, there is a strong competition between the M and O(I) phases. As a consequence, the GP constitutes a fingerprint for strong magneto-responsive properties in these family of compounds.\(^6,33,61,62\) In the case of Co substituted Gd$_5$Si$_2$Ge$_2$ compounds, the substitution of Co at the Si site results in the decrease of Si concentration in the system resulting in more dilution of the system. With increase in Co substitution, there is an increase in the O(I) component. As a result, due to the presence of two different phases coexisting in the system, nanometric regions of orthorhombic character with strengthened FM interactions are likely to be formed. These nanometric clusters with enhanced FM interactions are responsible for the appearance of GP. The decrease in $T_C$ with Co substitution is attributed to the increase in Ge concentration in the matrix phase, which results in the rupturing of inter-slab bonds due to the large size of Ge resulting in the decrease of magnetic exchange interactions and consequently a decrease in $T_C$ is observed.

Usually, the susceptibility of a GP at low fields follows the power law

$$\chi^{-1}(T) \propto \left(\frac{T}{T_R^{C}} - 1\right)^{-\lambda}$$

where $\lambda$ is the magnetic susceptibility exponent ($0 \leq \lambda < 1$) and $T_R^{C}$ is the random critical temperature.\(^{38,39}\) $T_R^{C}$ is taken as the temperature for which the equation yields a $\lambda$ ($\lambda_{pm}$) value close to zero above $T_o$. The linear part of the plot $\ln(\chi^{-1})$ vs. $\ln(T/T_R^{C} - 1)$ is fitted with the power law, and the estimated susceptibility exponent values are shown in Fig. 9. The value of $\lambda$ lies in between 0 and 1 and decreases with increase in the field, a signature of GP. This behaviour is seen in similar compounds such as Tb$_5$Si$_2$Ge$_2$\(^{38}\) and Gd$_5$Ge$_4$\(^{63}\) typical of short-range FM clusters in a PM matrix and is the hallmark of Griffith’s singularities. As the Co substitution increases from $x = 0.1$ to $x = 0.4$, it can be seen that the value of $\lambda$ also increases from 0.54 to 0.79 for 100 Oe and 0.31 to 0.61 for 10 000 Oe clearly suggesting an increase in the FM component within the PM matrix with Co substitution. The increase in the value of $\lambda$ for
Co substituted samples suggest an increase in the strength of GP. However, a thorough understanding of these short-range correlations would require small angle neutron scattering or muon spin rotation measurements.  

E. ESR studies

ESR is an effective tool to probe the local and microscopic magnetic states of materials. The ESR spectra of Gd$_5$Si$_{2-x}$Co$_x$Ge$_2$ were recorded at various temperatures and is presented in Fig. 10 as a representative of the series. It can be seen that the ESR spectrum is asymmetrically distorted below $T_C$. The temperature-dependent ESR results show that at high temperatures $T = 320$ K, the spectra show only one resonance with a well-characterized Lorentian line shape. In the intermediate temperatures 240 K $< T < 293$ K, there are two rather distinct lines and at low temperatures $T < 240$ K, the paramagnetic resonance peak vanishes completely. When approaching $T_C$, the ESR spectra show a small shift toward higher fields and becomes less asymmetrical. Above $T_C$, however, the spectra broaden and become more symmetrical with increasing temperature.  

The spectrum at 320 K shows a single resonance line with a Lorentzian shape at resonance field of 323 mT. When the temperature is lowered further, two resonance peaks appear, one at the higher resonance field corresponds to a PM phase and the other at a lower field corresponds to the FM phase. This is due to the appearance of short-range spin ordering or FM magnetic clusters between $T_N$ and $T_C$. As the temperature is decreased further, FM correlations grow at the expense of PM interactions and a complete PM–FM transition occurs below $\sim 280$ K. This is designated by the shift of the shoulder toward further lower-field region of the spectrum.

F. Isothermal magnetization measurements and magnetocaloric effect

Isothermal magnetization measurements were carried out in the temperature range of 200–320 K with a temperature interval of 5 K for the alloy samples with $x = 0.1$, 0.2 and 0.4. For the magnetization measurement at a particular temperature, the field was swept from 0–50 kOe and back to 0 Oe, and the results are shown in Fig. 11(a)–(c). It is evident from the $M(H)$ curves that the magnetization decreases with increase in temperature and becomes linear in $H$ as the temperature exceeds the magnetic ordering temperature. It can be noted from Fig. 11(a)–(c) that, there is a considerable magnetic hysteresis in the vicinity of the ordering temperature, signifying that FOPT is inherent in the system. This hysteresis is due to a field induced first order crystallographic phase change from monoclinic PM phase to O(1) FM phase. It can be seen that this field-induced phase transition reverses upon decreasing the field, but with some hysteresis around the transition region. This feature further suggests the reversible character of the structural transition, at which the structure of the alloy returns to its initial state once the magnetic field is completely removed. It can be seen that the hysteresis is maximum in the vicinity of $T_C$, where the structural transition occurs. However, it should be noted that in addition to FOPT, second order phase transition (SOPT) is also present in the system as is evident from the $M-T$ curves. The XRD results also confirm the co-existence of monoclinic and O(1) phases in the system. It can be seen that with increase in Co concentration, there is a reduction in the thermal hysteresis. This is attributed to the increase in the O(1) component, which is responsible for reducing the first order nature of the phase transition. Thus, Co substitution at the Si site favors the formation of the O(1) phase, thereby reducing the hysteresis loss. The Arrott plots ($M^2$ versus $H/M$) for all the compositions with $x = 0.1$, 0.2 and 0.4 are plotted in Fig. 11(d)–(f). According to the Banerjee criterion, the order of magnetic transition can be determined from the slope of the isotherm plot. The negative slope in the Arrott plots is a clear indication of the presence of first-order phase transition in these compounds while a positive slope corresponds to a second order transition. For $x = 0.1$ and $x = 0.2$, the Arrott plots indicate a negative slope confirming that first order nature of phase transition is present while for $x = 0.4$, the Arrott plots clearly show the transformation from first order to second order. Hence, it can be acclaimed that as Co concentration increases, the compounds mainly stabilise in the O(1) phase indicating that second order transition is more likely to take place.

The magnetocaloric effect in these compounds has been evaluated from the isothermal magnetization data using the thermodynamic Maxwell relations. Fig. 12(a)–(c) represent the change in magnetic entropy ($\Delta S_M$) as a function of temperature under different magnetic fields for $x = 0.1$, 0.2 and 0.4 respectively. All the curves show a broad maximum of $-\Delta S_M$ around their respective $T_C$. The value of $-\Delta S_M$ peak increases with the field and the peak position remain nearly unaffected. Under a magnetic field variation of 50 kOe, the maximum magnetic entropy change for Gd$_5$Si$_{2-x}$Co$_x$Ge$_2$ are 9, 8.5 and 4.2 J kg$^{-1}$ K$^{-1}$ for $x = 0.1$, 0.2 and 0.4 respectively. It can be seen that with increase in Co substitution, the $-\Delta S_M$ peak broadens. Also, there is a reduction in the magnetic entropy change with increase in Co substitution. This is attributed to the presence of combined phases in the system and the increase of the O(1) component with increase in Co concentration. MCE is positive.
over the entire temperature range as in the case for FM materials because of magnetic ordering phenomenon with the application of the magnetic field. However, it can be seen that even though there are two transitions in the magnetization measurements, the magnetic entropy change is concentrated only in the vicinity of the first order transition region. This suggests that the entropy change associated with the second order phase transition is negligible and the isothermal entropy change is maximum around the first order transition region.

Refrigerant capacity is a crucial parameter which determines the cooling capacity of a magnetocaloric material and indicates how much heat can be transferred from the cold end ($T_1$) to the hot end ($T_2$) of the refrigerator in one ideal thermodynamic cycle for a magnetic field change of $\Delta H$ and is defined as:

$$RC = -\int_{T_1}^{T_2} \Delta S_m(T) \Delta H dT$$

where $\Delta S_m(T)$ is the isothermal entropy change. Another critical parameter which determines the cooling efficiency of a magnetic refrigerant material is the relative cooling power (RCP) which is the measure of the amount of heat that can be transferred.

Fig. 11  Field dependence of magnetization at different temperatures for Gd$_{5}$Si$_{2-x}$Co$_x$Ge$_2$ (a) $x = 0.1$, (b) $x = 0.2$ and (c) $x = 0.4$ and the Arrott plots for (d) $x = 0.1$, (e) $x = 0.2$ and (f) $x = 0.4$. 
between the cold and hot reservoirs in an ideal refrigeration cycle and is expressed as

\[
\text{RCP} = -\Delta S_{\text{M}}^{\text{max}} \delta T_{\text{FWHM}}
\]

where \(\delta T_{\text{FWHM}}\) is the full width at half maximum of the \(\Delta S_{\text{M}}-T\) curve.

The RC values obtained for \(x = 0.1, 0.2\) and \(0.4\) for a field change of 50 kOe are 200, 185 and 75 J kg\(^{-1}\). The RCP values obtained for \(x = 0.1, 0.2\) and 0.4 for a field change of 50 kOe are 257, 204 and 106 J kg\(^{-1}\) respectively. It is to be noted that the hysteresis loss has been accounted while calculating the effective RC and RCP. The variations of effective RC and RCP as a function of field are shown in Fig. 12(d). The transition temperatures, thermal hysteresis, magnetic hysteresis, entropy changes, and the effective RC and RCP values are tabulated in Table 3. Co substituted compounds exhibit much higher RCP values and their operating temperature could be tuned to the desired temperature, suggesting that these compounds could be used for sub-room temperature magnetic refrigeration applications.

A new criterion based on the universal curve has been proposed for determining the order of phase transition based on the re-scaling of magnetic entropy change curves.\(^{69-71}\) The phenomenological universal curve can be calculated from purely magnetic measurements and results in the collapse of entropy change curves after a scaling process, regardless of the applied magnetic field. Hence, the major assumption is based on the fact that if a universal curve exists, then the equivalent

**Table 3** Transition temperatures, thermal hysteresis, magnetic hysteresis, entropy changes, effective refrigerant capacity, and relative cooling power calculated for Gd\(_5\)Si\(_2\)\(_x\)Co\(_x\)Ge\(_2\)

<table>
<thead>
<tr>
<th>Transition temperature of M to O((i)) phase on field cooling (K)</th>
<th>Transition temperature of O((i)) to M phase on field warming (K)</th>
<th>Transition temperature of O((i)) phase on field cooling and warming (K)</th>
<th>Thermal hysteresis (K)</th>
<th>Magnetic hysteresis at 50 kOe (J kg(^{-1}))</th>
<th>(-\Delta S_{\text{M}}) (J kg(^{-1}) K(^{-1})) (\Delta H = 50) kOe</th>
<th>Effective RCP (J kg(^{-1})) (H = 50) kOe</th>
<th>Effective RC (J kg(^{-1})) (H = 50) kOe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>255</td>
<td>260</td>
<td>292</td>
<td>5</td>
<td>35</td>
<td>9</td>
<td>257</td>
</tr>
<tr>
<td>0.2</td>
<td>240</td>
<td>245</td>
<td>291</td>
<td>5</td>
<td>24</td>
<td>8.5</td>
<td>204</td>
</tr>
<tr>
<td>0.4</td>
<td>210</td>
<td>214</td>
<td>310</td>
<td>4</td>
<td>10</td>
<td>4.2</td>
<td>106</td>
</tr>
</tbody>
</table>
points of the $\Delta S_M(T)$ curves measured at different applied fields should collapse onto the same universal curve. For materials undergoing a second order phase transition, the rescaled magnetic entropy change for different applied fields collapse onto a single curve. However, for materials undergoing a first order phase transition, the rescaled $\Delta S_M$ curves do not follow the universal behaviour. As a result, the universal curve can be used as a method for distinguishing first and second order phase transitions. Fig. 13 shows the universal curve constructions for each sample by plotting the rescaled entropy change, $\Delta S_M/\Delta S_{M,\text{peak}}$, against the temperature variable, $\theta$ where $\theta$ is defined by:

$$\theta = \begin{cases} 
-(T - T_C)/(T_{r_1} - T_C) & T \leq T_C \\
(T - T_C)/(T_{r_2} - T_C) & T \geq T_C
\end{cases}$$

Here, the reference temperatures ($T_{r_1}$ and $T_{r_2}$) are chosen such that $\Delta S_M(T_{r_1})/\Delta S_M(T_{r_2}) = \Delta S_{M,\text{peak}}/2$.

In Fig. 13, it is evident that the curves do not collapse, for temperatures below $T_C$, indicating the first order nature of phase transition. For $x = 0.1$, the divergence of the curves above the $T_C$ is evident. As the cobalt concentration increases to $x = 0.4$, a gradual trend towards collapse can be seen which corresponds to the weakening of the first order transition. This is concordant with the trends observed in the Arrott plots shown in Fig. 11(d)-(f). Such a weakening of first order phase transition has been observed in manganites by chemical doping and with reduced dimensionality. In the range, $-1 < \theta < 0$, the collapse is real for second order transitions and is only apparent for first order transitions. For temperatures above $T_C$, it can be seen that the curves do not collapse for $\theta > 0$. For $\theta > 0$, the collapse of the curves is due to the paramagnetic behaviour. However, in the case of cobalt-substituted compounds, Griffiths-like phases exist in the system indicating the presence of FM clusters in the PM matrix. Hence, the universal curves of the cobalt-substituted samples do not collapse for temperatures above $T_C$, i.e. $\theta > 0$ indicating that some FM clusters exist in the PM matrix above $T_C$.

IV. Conclusion

In summary, the influence of Co substitution for Si on polycrystalline samples of Gd$_5$Si$_2$Co$_x$Ge$_2$ with $x = 0, 0.1, 0.2$ and $0.4$ has been investigated. X-ray diffraction studies together with ESR and magnetization measurements reveal a mixture of M and O(1) crystal structures at room temperature. Low field magnetization data taken in FCC and FCW mode shows the presence of two transitions, a FOPT and a SOPT for $x = 0, 0.1, 0.2$ and $0.4$. The structural transition is marked by a significant hysteresis between FCC and FCW measurements. The maximum $-\Delta S_M$ for Gd$_5$Si$_2$Co$_x$Ge$_2$ are $9, 8.5$ and $4.2$ J kg$^{-1}$ K$^{-1}$ for $x = 0.1, 0.2$ and $0.4$ for a field change of 50 kOe. The presence of Griffiths-like phase has been established, which can be a consequence of the strong correlation between the magnetic and atomic lattices and constitutes a fingerprint for strong magneto-responsive properties in this family of compounds. Universal curve analysis reveal a weakening of first order transition with increase in Co concentration.

Acknowledgements

The authors acknowledge CSIR 12th Five Year Plan Project, CSC0132 for financial support. Bhagya Uthaman is thankful to
KSCSTE and CSIR for granting the fellowship. Senoy Thomas acknowledges DST, India for the support via Inspire faculty award. The authors deeply acknowledge Prof. P. N. Santhosh, IIT Chennai for DSC measurements, Mr Ajeesh P. Paulose for PPMS measurements, Mr Kiran Mohan for TEM measurements, Mr C. K. Chandrakanth and Mr Harish Raj V. for SEM measurements.

References