

SCIENTIFIC REPORTS

OPEN

Griffiths phase behaviour in a frustrated antiferromagnetic intermetallic compound

Krishanu Ghosh¹, Chandan Mazumdar², R. Ranganathan² & S. Mukherjee¹

Received: 30 January 2015

Accepted: 25 September 2015

Published: 30 October 2015

The rare coexistence of a Griffiths phase (GP) and a geometrically frustrated antiferromagnetism in the non-stoichiometric intermetallic compound $\text{GdFe}_{0.17}\text{Sn}_2$ (the paramagnetic Weiss temperature $\theta_p \sim -59$ K) is reported in this work. The compound forms in the $Cmcm$ space group with large structural anisotropy ($b/c \sim 4$). Interestingly, all the atoms in the unit cell possess the same point group symmetry (Wyckoff position $4c$), which is rather rare. The frustration parameter, $f = |\theta_p|/T_N$ has been established as 3.6, with the Néel temperature T_N and Griffiths temperature T_G being 16.5 and 32 K, respectively. The T_G has been determined from the heat capacity measurement and also from the magnetocaloric effect (MCE). It is also shown that substantial difference in GP region may exist between zero field and field cooled measurements - a fact hitherto not emphasized so far.

In magnetic systems, it was shown that the observation of a Griffiths phase (GP)¹ may have many different origins, *e.g.*, phase separation, occurrence of clusters of sizes ranging from nanometers to micrometers², competing intra- and interlayer magnetic interaction, microtwinning, *etc.*³⁻⁵. Experimentally, most of the GP compounds are known to exhibit bulk ferromagnetic (FM) order. In some of the antiferromagnetic (AFM) compounds which show characteristic reminiscent of a GP^{6,7}, the paramagnetic Weiss temperature (θ_p) is found to be positive, suggesting the presence of strong FM interactions. The only GP compound known to us, that exhibits negative θ_p , is an oxide compound $\text{Ca}_3\text{CoMnO}_6$ ⁸. This implies that in most of the GP compounds the FM interactions compete quite strongly with dominant AFM interaction, resulting in positive θ_p . In order to realize the GP in an AFM system with $|\theta_p|/T_N < 1$, one needs to search for a system that has not only the favourable types of structural defects, but also should have the magnetic interaction of A-type ($\uparrow \downarrow \downarrow \uparrow$) or C-type ($\uparrow \uparrow \downarrow \downarrow$), where $J_{AFM}/J_{FM} > 1/2$, J being the exchange interaction⁸. Thus an appropriate choice of AFM compound that has suitable structural defects and the right kind of competing magnetic interaction, may lead us to a GP even in a geometrically frustrated magnetic (GFM) system. This work focuses on such problem, namely, to search for a geometrical frustrated antiferromagnet with a GP. This is yet to be realized in view of complex magnetic interactions in AFM intermetallic compounds.

It was earlier found that most of the $RETM_x\text{Sn}_2$ (RE = rare earths, TM = transition metals; $x < 1$) compounds form in a defect orthorhombic CeNiSi_2 -type crystal structure (space group: $Cmcm$)⁹ which is a filled variant of ZrSi_2 -type structure (space group: $Cmcm$). In both structures, all the atoms occupy distinct $4c$ Wyckoff positions ($0, y, 0.25$)⁹, and do not show any inter-element cross-substitutional effects¹⁰. While the CeNiSi_2 -type structure may be considered as an intergrowth of binary AlB_2 and ternary BaAl_4 -type slabs, the ZrSi_2 -type structure may be viewed as an intergrowth of binary AlB_2 and binary CaF_2 -type slabs. If all the transition metal atoms are removed from the ternary BaAl_4 -type segment it can be considered as a CaF_2 -type structure [see Fig. 1(a) of ref. 11]. The binary $RESn_2$ compounds form in the ZrSi_2 -type crystal structure¹²⁻¹⁵. In the complex solid solutions of $RETM_x\text{Sn}_2$ ($x < 1$) compounds, the transition metals are randomly distributed leaving many TM sites vacant^{12,16}. This, in turn, results in the local variation of RE - RE bond length¹¹. The random disruption of magnetic exchange

¹Department of Physics, The University of Burdwan, Golapbag, Bardhaman - 713104, West Bengal, India.

²Condensed Matter Physics Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India. Correspondence and requests for materials should be addressed to C.M. (email: chandan.mazumdar@saha.ac.in)

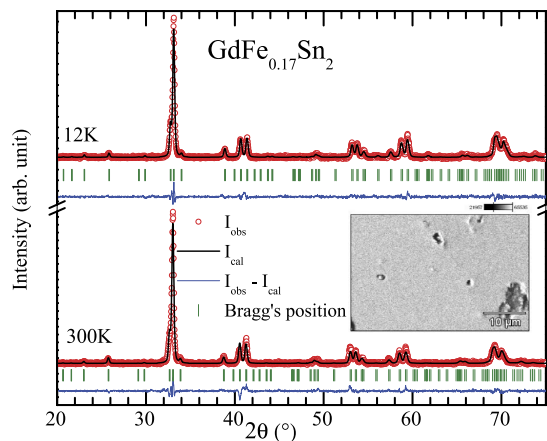


Figure 1. (Bottom) XRD pattern of $\text{GdFe}_{0.17}\text{Sn}_2$ measured at room temperature. The inset shows SEM image. (Top) XRD pattern of $\text{GdFe}_{0.17}\text{Sn}_2$ measured at 12 K.

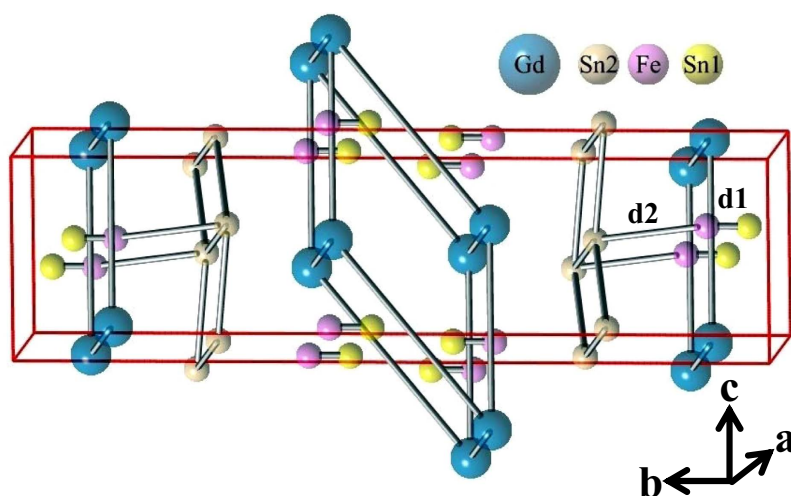


Figure 2. Crystallographic structure of $\text{GdFe}_{0.17}\text{Sn}_2$.

interaction caused by the varying bond lengths affects the long range magnetic order throughout the sample, but are expected to be found in many microscopically small regions inside the samples. According to the Griffiths model, the disorder driven random distribution of magnetic interactions result in different sets of exchange constants for different lattice points throughout the material^{1,17}. RETM_xSn_2 ($x < 1$) compounds that have the similar characteristics, therefore appear to be potential candidates for observing a GP. In the case of REFe_xSn_2 series ($\text{RE} = \text{Tb} - \text{Tm}$), it was shown earlier through neutron diffraction experiments that in addition to A- or C-type AFM ordering (favourable to a GP in AFM systems), the systems also have a sizeable number of frustrated rare earth ions, that ensures $|\theta_p| > T_N$ ¹⁸. In our quest to search for GP in a GFM intermetallic system, we have synthesized and studied the magnetic properties of $\text{GdFe}_{0.17}\text{Sn}_2$, a material that satisfies most of the above mentioned criteria. The Gd-based system ($L = 0$) was chosen due to its negligible magnetic anisotropy resulting from the higher order exchange interaction¹⁹.

Results and Discussion

The powder x-ray diffraction (XRD) patterns taken at room temperature of $\text{GdFe}_{0.17}\text{Sn}_2$ were analyzed by considering that the material has a CeNiSi_2 -type orthorhombic structure (space group: $Cmcm$). All the peaks in the XRD pattern could be indexed using this space group (Fig. 1, bottom). The lattice parameters, $a = 4.443(1)\text{\AA}$, $b = 16.43(1)\text{\AA}$ and $c = 4.371(1)\text{\AA}$ are close to that reported earlier for $\text{GdFe}_{0.17(2)}\text{Sn}_2$ ¹⁶. However, the full Rietveld analysis, allowing the variation of occupancy factor of Fe and Sn atoms, suggests the actual composition to be $\text{GdFe}_{0.19}\text{Sn}_{1.93}$. We find the average interatomic distances Fe-Sn1 (d1) as 0.9 Å, Fe-Sn2 (d2) as 3.1 Å and the angle Sn1-Fe-Sn2 as 135.2° (Fig. 2). In isostructural stoichiometric CeNiSi_2 , we find that the Ni-Si1 and Ni-Si2, distances are nearly identical, close to 2.31 Å.

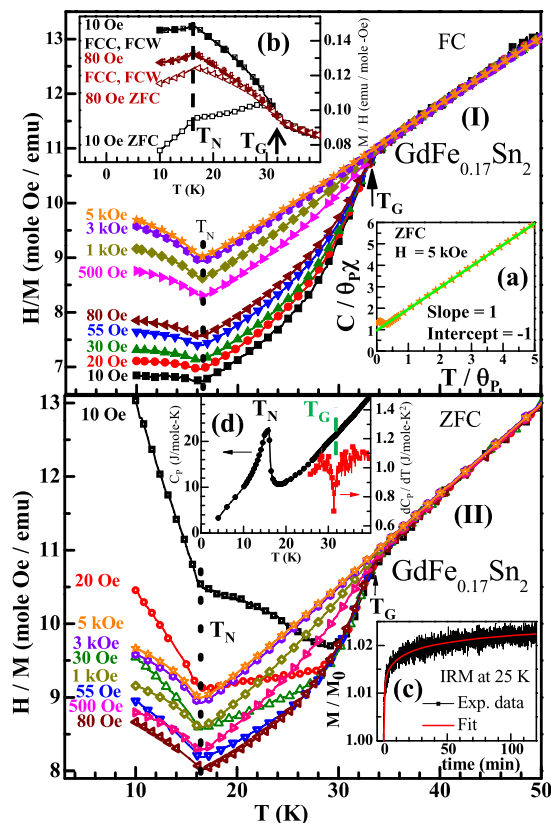


Figure 3. Temperature dependence of the inverse magnetic susceptibilities of $\text{GdFe}_{0.17}\text{Sn}_2$ measured at different externally applied magnetic field under FC (top-I) and ZFC (bottom-II) configuration during warming cycle; (Inset (a)): Normalized inverse susceptibility versus temperature at $H = 5$ kOe. C is the Curie constant and θ_p is the paramagnetic Weiss temperature; (Inset (b)): Magnetic susceptibilities of the same sample measured under ZFC, FCC and FCW conditions in fields of 10 and 80 Oe; (Inset (c)): Normalized magnetic relaxation data along with the fit of stretched exponential are presented. (Inset (d)): Temperature dependence of heat capacity in absence of any magnetic field is shown using the left side axis. The anomaly observed due to GP transition can be observed more clearly by taking derivative of the heat capacity around T_G as shown using the right hand axis of the inset.

The Sn1-Fe-Sn2 angle in $\text{GdFe}_{0.17}\text{Sn}_2$ is also found to be quite stretched in comparison to that found in CeNiSi_2 , where the Si1-Ni-Si2 angle is close to 117.7° ²⁰. Shorter average interatomic distances (Fe-Sn1) generally reflect the presence of vacancies (Fe and/or Sn) in the crystal structure, and earlier reported in quite a few RETM_xSn_2 series of compounds ($\text{TM-Sn} \sim 2\text{--}2.5 \text{ \AA}$)^{12,21}. The scanning electron microscope (SEM) picture (Fig. 1; (bottom: inset)) and energy dispersive analysis of X-ray (EDAX) suggest an essentially single phase nature with average composition as $\text{GdFe}_{0.19}\text{Sn}_{1.91}$ which is close to the value obtained through Rietveld analysis. The diffraction patterns taken at lower temperatures do not suggest any major structural phase transformation (Fig. 1; top).

The magnetic susceptibility (χ) measurements (2–300 K) under the influence of external magnetic field, in excess of 5 kOe, suggest that the compound orders magnetically at ~ 16.5 K (Fig. 3). The negative value of θ_p (-59 K), estimated from inverse magnetic susceptibility in the paramagnetic region and the absence of spontaneous magnetization in the Arrott plot (M^2 vs. H/M)²² (Fig. 4; inset (b)), suggest that $\text{GdFe}_{0.17}\text{Sn}_2$ orders antiferromagnetically at $T_N \sim 16.5$ K. The isothermal magnetizations measured below T_N , do not exhibit any hysteresis behaviour and have a near linear magnetic field dependence, as expected for an AFM system (Fig. 4) (Fig. 4; inset (a)).

The estimated value of frustration parameter, $f = |\theta_p|/T_N = 3.6$, suggests that this compound is a frustrated magnetic system (Fig. 3; inset(a)), as per the criterion suggested by A. P. Ramirez²³. This magnetic frustration has its origin in the crystal structure itself. In the CeNiSi_2 -type crystal structure, the rare earth ions are arranged as infinite sheets of face-sharing RE_6 trigonal prisms, and also as RE_4 tetrahedrons stretched along [010]¹⁸. The neutron diffraction measurements on REFe_xSn_2 ($\text{RE} = \text{Tb} - \text{Tm}$, $0.1 < x < 0.15$) had earlier established an A- (or C-) type AFM structure where some of the rare earth ions occupying the position of the trigonal faces of the prism and/or in the tetrahedron exhibiting frustration of the magnetic moments [see Fig. 4(b), 7(b), 11(b) of ref. 18]. This is in agreement with the fact that these compounds also have frustration parameter $f \sim 2\text{--}3$ ¹⁸, similar to that observed in $\text{GdFe}_{0.17}\text{Sn}_2$.

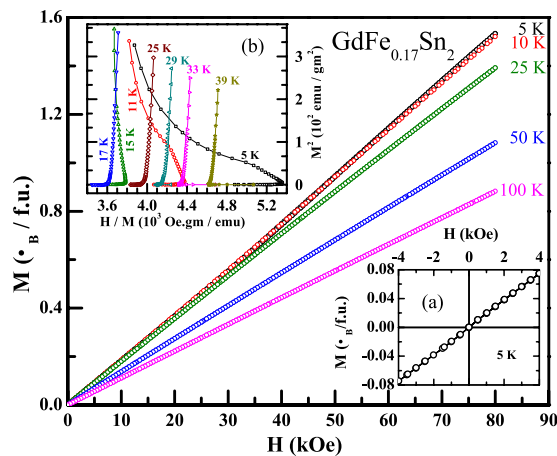


Figure 4. Isothermal magnetization at different temperatures of $\text{GdFe}_{0.17}\text{Sn}_2$ are presented for $0 \leq H \leq 80$ kOe. (Inset (a)): All the isothermal magnetization measurements were performed up to a range of ± 80 kOe. Here, only the data in only the range of $-5 \leq H \leq 5$ kOe measured at 5 K are shown. (Inset (b)): Arrott plot in the temperature range 5–39 K.

The origin of magnetic frustration in REFe_xSn_2 ($\text{RE} = \text{Tb} - \text{Tm}$, $0.1 < x < 0.15$) primarily depends on the crystal structure. Therefore $\text{GdFe}_{0.17}\text{Sn}_2$, being in the same crystallographic structure, is also expected to possess geometrically frustrated magnetic moments. The magnetic structure of $\text{GdFe}_{0.17}\text{Sn}_2$, however, has not been directly checked using neutron diffraction technique due to the large cross-section of neutron absorption of Gd.

The value of effective magnetic moment per formula unit (μ_{eff}) calculated from the inverse magnetic susceptibility in the paramagnetic range found to be $8.19\mu_B$ which is slightly higher than that of free Gd^{3+} ions ($7.94\mu_B$). One may attribute the origin of larger moment as due to the Fe atoms present in this compound. Here, it may be noted that the values of μ_{eff} for all other members of the series REFe_xSn_2 ($\text{RE} = \text{Tb} - \text{Tm}$, $0.1 < x < 0.15$) are also reported to be higher than that of their corresponding free ion values, where neutron diffraction measurements failed to detect any ordered moment of Fe^{18} . Additionally, GdSn_2 that forms in the same space group ($Cmcm$), also exhibits μ_{eff} of similar magnitude ($8.16\mu_B$)²⁴. Therefore, in our opinion, the slightly larger value in μ_{eff} observed in our compound might originate from the positive polarization of conduction electrons²⁴, or as A. P. Ramirez suggested, due to the reduction of moment density (resulting in an increase of effective magnetic moment) generally found in frustrated magnetic systems²³.

The susceptibility (χ), however, measured at a field lower than 5 kOe, both in zero field cooled (ZFC) and field cooled (FC) configuration suggests the presence of another anomaly around 32 K (Fig. 3; inset (b)). The field cooled magnetic susceptibilities do not show any remanence while measuring during cooling (FCC) and subsequent warming (FCW) (Fig. 3; inset (b)). We first discuss the magnetic susceptibility measurements in FC configuration. The ZFC measurement and presence of thermoremanent behaviour in low field will be discussed later.

The inverse FC magnetic susceptibility ($H < 5$ kOe), in the paramagnetic region ($T > T_N$) shows a downward deviation from linearity below a temperature, $T_G \sim 32$ K (Fig. 3; I). As the applied external magnetic field increases gradually from 10 Oe onwards, the extent of deviation in magnetic susceptibility systematically diminishes until a Curie-Weiss (CW) behaviour is observed down to T_N , for a field in excess of 5 kOe (Fig. 3; I). The deviation from CW behaviour at a low measuring field, while approaching the ordering temperature (T_C or T_N) from above (at T_G), may be attributed due to the presence of small clusters in addition to the paramagnetic matrix. The downward deviation in $\chi^{-1}(T)$ results from an enhancement in χ due to the contribution from the FM clusters. The deviation is suppressed in large magnetic field due to the polarization of spins outside the clusters. To establish the presence of magnetic clusters in $\text{GdFe}_{0.17}\text{Sn}_2$, we have also performed spin relaxation measurements by studying the Isothermal Remanent Magnetization (IRM) in the GP region. The magnetization exhibits a relaxation behaviour, that can only be fitted well using a stretched exponential form, $M(t) \sim \exp\left(-\frac{t}{\tau}\right)^\beta$; ($0 < \beta < 1$) below T_G , with $\beta \sim 0.45$ (Fig. 3; inset (c)), often observed in the systems containing magnetic clusters^{25,26}. This FM-like anomaly at 32 K cannot be attributed to the structurally related compound GdSn_2 , even if it is present in our compound below the resolution limit of XRD, as it orders antiferromagnetically at 27 K²⁴. It may be noted here, in the case of $\text{ThFe}_{0.2}\text{Sn}_2$, the cross-substitution effect of different constituent elements had been categorically ruled out through the ^{57}Fe and ^{119}Sn Mössbauer spectroscopy measurements¹⁰. It is therefore quite unlikely that any such cross-substitution would occur in the isostructural

GdFe_{0.17}Sn₂ system as well. Thus, the anomaly at 32 K appear to be an inherent characteristic of GdFe_{0.17}Sn₂.

The phenomena observed in the magnetic susceptibility of GdFe_{0.17}Sn₂ can be explained using a model proposed by Griffiths¹. In the GP model, the long-range ordering temperature, $T_C(x)$, of a randomly diluted ferromagnet will be lower than the same of the undiluted one ($T_C^{undiluted}$). The thermodynamic properties (e.g. magnetization) will be non-analytical in this region ($T_C(x) < T < T_C^{undiluted}$) due to the formation of a low density clusters with short-range ordering. Here $T_C^{undiluted}$ is the temperature at which this GP forms and is popularly known as the Griffiths temperature (T_G). The temperature range between T_C and T_G corresponds to a GP, and this GP is different from the paramagnetic as well as the long-range FM phase. Though the typical behaviour of a GP are already reported in several compounds^{5,8,17,27}, the direct confirmation of GP in any system is really a difficult task¹⁷.

One indirect way to confirm whether the short-range FM correlations observed in the PM state can be ascribed to the GP is the deviation of magnetic susceptibility for $T \ll T_G$. χ^{-1} in such case should generally follow power law behaviour describing the Griffith singularity²⁸

$$\chi^{-1} \propto (T - T_C^R)^{1-\lambda}, \quad (1)$$

where λ is the magnetic susceptibility exponent, and T_C^R is the critical temperature of random ferromagnetic clusters where susceptibility tend to diverge. In most of the GP compounds reported so far, the magnetic transition temperature (T_G or T_N) and T_C^R found to be very close^{5,17,29,30}. However, for an AFM system, where $\theta_p < T_N$, one is constrained to test the validity of the power law behaviour close to T_N only, instead of a region close to T_C^R . However, in cases where $|\theta_p|/T_N > 1$ and $T_N \sim T_G$, i.e., $(T_N - T_C^R)/(T_G - T_C^R)$ is quite high (> 0.5), the temperature region available for testing the applicability of this power law turns out to be closer to T_G , than to T_C^R , and in such cases, the above mentioned power law cannot be applied. The large value of $(T_N - T_C^R)/(T_G - T_C^R) \sim [16.5 - (-59)]/[32 - (-59)] = 0.83$, estimated in the case of GdFe_{0.17}Sn₂, restricts the applicability of the above mentioned power law behaviour in the present case. Although we also observed that the behaviour of $\chi^{-1}(T)$ in the temperature range, $T_N < T < T_G$, is similar to GP, or more accurately, a system having FM clusters in a temperature range above the long range magnetic ordering temperature. It may be noted here that the only other oxide GFM that also exhibits GP behaviour, Ca₃CoMnO₆, has similar values of f (~ 3.8), θ_p (-50 K) and T_N (~ 13 K), but the much larger value of T_G (~ 125 K) ensures that eq. (1) can be applicable close to T_N in that compound $[(T_N - T_C^R)/(T_G - T_C^R) \sim 0.36]^8$, unlike in the present case of GdFe_{0.17}Sn₂.

In order to demonstrate the existence of a GP in our system, we should look into the possible reason behind the formation of such clusters. In GdFe_{0.17}Sn₂, only 17% of the transition metal-sites are randomly occupied with Fe atoms and the rest are vacant. This creates a local disorder in the crystal structure. As mentioned earlier, the presence of these vacancies are also reflected in the estimated shortened average bond lengths^{12,21}. The random presence of vacancies in the transition metal site decreases the Gd³⁺-Gd³⁺ interionic distance locally¹¹ and thereby introduces a random spatial variation of the exchange interaction (J) in the bonds between Gd³⁺ ions on a regular lattice³¹. This results in the coexistence of two phases with different J values within the same crystalline phase. In the first phase, the Fe-sites are vacant and this forms the major phase, while the minor phase, containing Fe atoms at the transition metal-sites, are randomly distributed within the major phase¹². Similar coexistence of magnetic phases has already been observed in isostructural CeNi_{0.84}Sn₂³². In the original work of Griffiths, it was shown that, if a great enough fraction, $x > x_c$, of the bonds of a ferromagnet have $J = 0$, then a GP will form in the temperature range, $T_C < T < T_G$, with non-analytic free energy in an external magnetic field. The observation of a GP is possible in a system where the random disorder results in random spatial variation of J . The effect of disorder is to partition the pure system into small FM clusters. The disorder also needs to be quenched²⁵. The disorder is quenched in our system also, since the Fe atoms occupying the transition metal sites are fixed in the lattice. In GdFe_{0.17}Sn₂, it will be therefore justified to associate the major phase having vacant Fe-sites with long range AFM ordered state. The minor phase results from the random dilution of the AFM exchange interaction and is distributed in isolated small-sized FM clusters having positive J value. It may be pertinent to note here that in case of perovskite ruthenates, the variation of bond angle are argued to be responsible for observation of a GP³³. Thus, intermetallic GdFe_{0.17}Sn₂ appear to be one of the rare breed of compounds, apart from the oxide Ca₃CoMnO₆, to exhibit GP characteristics in an otherwise GFM material.

In order to study the change in magnetic entropy, if any, due to the FM ordering of such a small volume fraction of material, we have also made a careful study of the heat capacity as well as the magnetocaloric effect (MCE) close to T_G . The heat capacity of GdFe_{0.17}Sn₂ shows a large peak around 15.9 K, close to T_N (Fig. 3; inset (d)). The magnetic contribution to entropy at T_N , estimated from the heat capacity data, is found to be only $\sim 1.7R$, instead of the theoretically expected value of $2.09R$ ($R =$ universal gas constant). The reduced value of magnetic entropy suggests that nearly 20% of Gd-ions do not take part in long range ordering. Surprisingly, we find that the magnetic entropy associated with FM clusters in the GP, however insignificant, also leaves its imprint in heat capacity results, exhibiting a discernible anomaly close to $T_G \sim 32$ K (Fig. 3; inset (d), right axis).

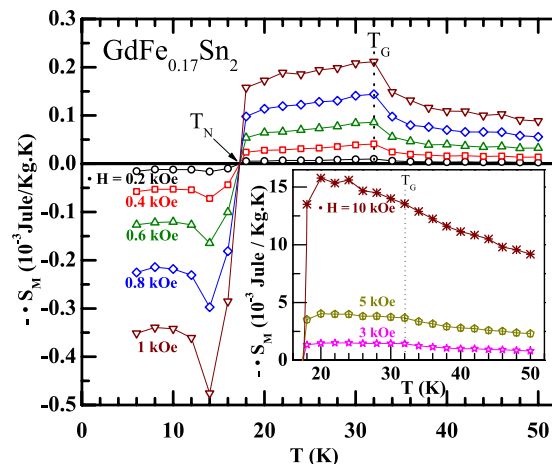


Figure 5. Magnetic entropy, estimated from low field isothermal magnetization measurements. (Inset): The magnetic entropy measured at higher magnetic fields.

The presence of FM-like spins within the clusters can also be confirmed through low field MCE measurements, that tracks the associated entropy change due to GP ordering. Although the volume fraction responsible for the GP is small, nevertheless the isothermal magnetic entropy (ΔS_M) measured at low field, unambiguously show a reduction in value below T_G (Fig. 5). The values of ΔS_M have been calculated from magnetization isotherms using the Maxwell thermodynamic relation,

$$\Delta S_M = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T} \right) dH \quad (2)$$

Close to T_G , $\Delta S_M(T)$ exhibits an well-defined peak, often seen in materials with ferromagnetic type ordering. Similar to the reduction in excess magnetization below T_G with the increase of magnetic field, the peak in MCE also gets suppressed for a magnetic field larger than 5 kOe (Fig. 5; inset). To the best of our knowledge, probing of a GP through MCE has not been reported earlier in literature.

We now focus on the ZFC magnetization measurement, which particularly at very low field, exhibit a markedly different nature to that which was commonly observed in FC measurements. While the FC magnetization tends to saturate at lower temperature ($T_N < T < T_G$), the low field ZFC measurements yield very small moment values, that rise with increasing temperature until reaching some maximum value below T_G , and then follow the FC susceptibility for higher temperatures (inverse susceptibility as shown in Fig. 3; II). As the applied magnetic field strength increases gradually, the thermoremanence decreases, and for magnetic fields higher than 500 Oe, the thermoremanence becomes barely discernible. Such thermoremanence behaviour are generally reported in spin-glass type compounds due to the presence of metastable states³⁴ or in anisotropic ferromagnets³⁵ due to the competing interactions of magnetic coupling energy and anisotropy energy. Although a few GP compounds, *e.g.*, Gd_5Ge_4 , have also been reported to exhibit thermoremanent behaviour⁵, such a strikingly different behaviour of ZFC and FC magnetization has not been reported earlier for any GP compound. Our result thus shows that the typical signature of GP, generally observed through FC measurements, may yield different character when measured in ZFC configuration.

In conclusion, we have shown that the intermetallic compound $GdFe_{0.17}Sn_2$ can be considered as a unique system that orders antiferromagnetically with geometric frustration ($f = |\theta_p|/T_N = 3.6$), and exhibits features similar to that observed in a GP. Only one oxide compound, Ca_3CoMnO_6 , has been reported earlier to have similar features⁸. We have found that the variation of magnetic susceptibility with field in the GP region may depend considerably on the measurement protocol, *i.e.*, ZFC and FC measurements, due to the metastable states of the spins involved in the GP. Such magnetic thermoremanent behaviour had not been reported earlier in any GP compounds. We have also shown that beside the magnetic susceptibility, GP ordering temperature can also be probed through both the MCE as well as the heat capacity measurements.

Methods

A number of polycrystalline compounds having nominal composition $GdFe_{0.17}Sn_2$ were melted in a water cooled arc furnace in the flowing argon atmosphere. The samples were melted several times to ensure homogeneity. The resultant ingots were then wrapped in Ta-foil and annealed under vacuum at 800 °C for 15 days. Powder x-ray diffraction (XRD) measurements were performed in the temperature range of 12–300 K using a 18 kW rotating anode diffractometer (Model: TTRAX-III, M/s Rigaku Corp., Japan). The single phase nature as well as lattice parameters were ensured through the Rietveld refinement

analysis using FULLPROF software³⁶. Magnetic [M (T, H, time)] and heat capacity (in the absence of external magnetic field) measurements were performed in the temperature range 2–300 K using a commercial SQUID-VSM and PPMS Evercool-II (M/s Quantum Design Inc., USA). The Scanning Electron Microscope (SEM) (S-3400N; M/s Hitachi, Japan) and energy dispersive analysis of X-ray (EDAX) (M/s Thermo Electron Corp. USA) measurements were also performed to check the spatial homogeneity and elemental composition of the system. The Isothermal Remanent Magnetization (IRM) measurements were carried out using the following protocol: the sample was cooled in the absence of magnetic field ($H = 0$) from room temperature to a temperature (25 K) below T_G . Then, with a waiting time $t_w = 0$ sec, the magnetic field was switched on and allowed to reach a value of 50 kOe. Once the magnetic field reaches 50 kOe, the field was switched off after $t_w = 0$ sec. As soon as the magnetic field diminishes to 0, the time dependence magnetization measurement was carried out, again after $t_w = 0$ sec.

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Acknowledgements

We thank Dr. R. Gopalan and Dr. Kavita of ARCI, Hyderabad, for SEM and EDAX measurement and Mr. Niraj Chaubey for initial support during sample synthesis. KG also thanks University Grants Commission, India for financial support. The work at SINP has been supported through CMPID-DAE project.

Author Contributions

R.R., C.M. and S.M. developed the concept of the study. K.G. synthesized the sample, performed the experiments and interpreted the data.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Ghosh, K. *et al.* Griffiths phase behaviour in a frustrated antiferromagnetic intermetallic compound. *Sci. Rep.* **5**, 15801; doi: 10.1038/srep15801 (2015).



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