Unusual magnetic properties of (Er$_{1-x}$Gd$_x$)$_5$Si$_4$ compounds

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Magnetic and magnetocaloric properties of polycrystalline (Er$_{1-x}$Gd$_x$)$_5$Si$_4$ with x=0.1 and 0.25 have been studied. The temperature dependencies of the dc magnetization and ac susceptibility indicate two magnetic transitions: the high temperature transitions are antiferromagnetic in character, whereas the low temperature ones are of ferromagnetic nature. The isothermal magnetization of these compounds shows metamagneticlike transitions at 5 K and no saturation in fields up to 70 kOe. Time dependencies of the magnetization data below the Néel temperature exhibit unusually strong relaxation effects with logarithmic time dependence. The ac susceptibility data reveal that magnetic state of these compounds is distinctly different from spin glasses and the relaxation behavior seen in the magnetization data is a consequence of complex magnetic interactions. The existence of complex magnetic interactions leads to an easy formation of field induced short range ferromagnetic correlations in the paramagnetic state and greatly affects both the magnetic and magnetocaloric properties of these compounds.

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I. INTRODUCTION

A rich variety of magnetic phenomena exhibited by rare earth (R) intermetallic compounds makes them promising candidates for fundamental studies as well as for numerous applications based on large magnetostriction (MS), magnetoresistance (MR) and magnetocaloric effects (MCEs).[1–4] Applications based on these unusually strong responses are still in their infancy, and therefore, materials with large values of the MS, MR, and MCE are of great interest. It is over a decade now since the first observation of the giant MCE, resulting from concomitant magnetic and structural transitions, in the intermetallic compound Gd$_5$Si$_2$Ge$_2$ near its ferromagnetic transition temperature ($T_C \cong 270$ K) was reported.[5] Since then, there has been a tremendous expansion of activity in the field of MCE in general and on the study of the magnetothermal properties of materials with coupled magnetic and structural transitions in particular.[6–12]

The intermetallic compound Gd$_5$Si$_2$Ge$_2$ belongs to the family of R_5T_4 (R=rare earth and T=Si and/or Ge) materials. Among the various members of the R_5T_4 family, owing to the occurrence of the giant MCE, the giant magnetoresistance, and colossal magnetostriction, the compounds with R=Gd have been studied quite extensively.[13–18] Most of the R_5T_4 compounds posses layered structures made up of the nanometric slabs. Each slab is constituted from five atomic monolayers of R and T atoms. It is the rearrangement of these slabs via changing specific $T–T$ bonds, which gives rise to different crystal structures adopted by this family of compounds.[14,18] Compounds with all the slabs connected through strong $T–T$ bonds adopt the Gd$_5$Si$_4$-type orthorhombic structure (also referred to as O-I type structure, space

group *Pnma*), whereas those without any interslab $T–T$ bonding posses the Sm$_5$Ge$_4$-type structure (referred to as O-II structure, space group *Pnma*). The compounds with alternate slabs connected through the $T–T$ bond belongs to the Gd$_5$Si$_2$Ge$_2$-type monoclinic structure (also known as M type, space group $P112_1/a$). During magnetostructural transitions exhibited by many members of the R_5T_4 series, the interslab bonding arrangement changes, whereas the intraslab bonds remain intact.[14,15,18]

Although the magnetic and structural transitions in the Gd based R_5T_4 compounds have been found to be coupled, there are a few reports in the literature which show that some members of the family exhibit decoupled magnetic and structural transitions.[19–21] For example, unlike the case of Gd$_5$Si$_2$Ge$_2$, where the coupled magnetostructural transition from the M paramagnetic phase to the O-I ferromagnetic phase occurs at ~270 K, the compound Tb$_5$Si$_2$Ge$_2$ has a magnetic ordering transition at ~110 K and a structural transition at ~100 K.[19] In Er$_5$Si$_4$, the structural and magnetic transitions are reported to be unusually far apart, i.e., they are separated by a temperature difference of ~200 K (the structural transition at ~230 K and the magnetic one at ~30 K).[20] Furthermore, in contrast to R_5Si$_2$Ge$_2$ compounds with R=Gd and Tb, the paramagnetic state of Er$_5$Si$_4$ is reported to be orthorhombic, whereas the magnetically ordered ground state is monoclinic.[20] Owing to presence of these anomalous properties, the compound Er$_5$Si$_4$ recently drew considerable attention.[20,22–28] The latest investigations have revealed that the magnetic state of Er$_5$Si$_4$ is sensitive to external parameters such as the magnetic field and pressure.[22,23,25–27] Studies of magnetic properties, heat capacity, and magnetostriction of Er$_5$Si$_4$ have shown that the compound exhibits structural transitions in the magnetically or-

dered state as well as within the paramagnetic state.[20,25,26] Neutron diffraction measurements, both under the applied magnetic field and hydrostatic pressure, have also shown that these external parameters cause a partial monoclinic to orthorhombic structural transition in the magnetically ordered state.[25,26] The noncompletion of this structural transition has been attributed to a strong single ion anisotropy associated with the Er^{3+} ion.[25]

In view of an unusual sensitivity of the magnetic and structural behaviors of Er_5Si_4 to magnetic field and pressure, we have studied the effects of partial substitution of Er by Gd on the magnetic and magnetocaloric properties of Er_5Si_4, and the results are presented in this paper. Similar to Er_5Si_4, the $(Er_{1-x}Gd_x)_5Si_4$ compounds with $x=0.1$ and 0.25 crystallize in the Gd_5Si_4-type structure. However, partial replacement of Er by Gd leads to the suppression of the orthorhombic to monoclinic transition seen at ~230 K in pure Er_5Si_4. The Gd substituted compounds show two magnetic transitions: the high temperature transition is antiferromagnetic in character, whereas the one at low temperature is ferromagneticlike. The analysis of the magnetization data indicates coexistence of both the ferromagnetic and antiferromagnetic correlations which leads to an unusually potent magnetic relaxation in these compounds.

II. EXPERIMENTAL DETAILS

The $(Er_{1-x}Gd_x)_5Si_4$ alloys with $x=0.1$ and 0.25 weighing 5 g each were prepared by arc melting of the stoichiometric quantities of the constituent elements on a water cooled copper hearth. The Er and Gd used in the present study were prepared by the Materials Preparation Center[29] at Ames Laboratory. Er was 99.86 at. % (99.99 wt. %) pure, whereas Gd was 99.5 at. % (99.95 wt %) pure. The Er contained the following major impurities in the ppm atomic (and in ppm by weight); O, 400 (38); C, 278 (20); F, 123 (14); N, 72 (6); H, 166 (1); and Fe, 30 (10). In Gd, the major impurities were O, 3047 (310); C, 1741 (133); and N, 191 (17). The Si was obtained from Cerac Inc., USA and was better than 99.999 wt % pure.

The structural analysis of the samples was performed by collecting x-ray powder diffraction patterns using Cu $K\alpha$ and Mo $K\alpha$ radiations at room temperature. Full profile refinement of the powder diffraction patterns was carried out using RIETICA.[30] Both ac and dc magnetic measurements, in the temperature range of 2–300 K and up to a maximum dc field of 70 kOe, were performed using the superconducting quantum inference device magnetometer (MPMS XL, Quantum Design, USA). The temperature dependent magnetization data in various applied magnetic fields were collected under zero field cooled (ZFC), field cooled cooling (FCC), and field cooled warming (FCW) conditions. In the ZFC mode, the samples were cooled from the room temperature to 2 K and the magnetization data were collected on warming after the application of the magnetic field at the lowest temperature, whereas during the FCC mode, the magnetic field was applied at room temperature and the $M(T)$ data were collected during the cooling. During FCW condition, the samples were cooled to the lowest temperature in the pres-
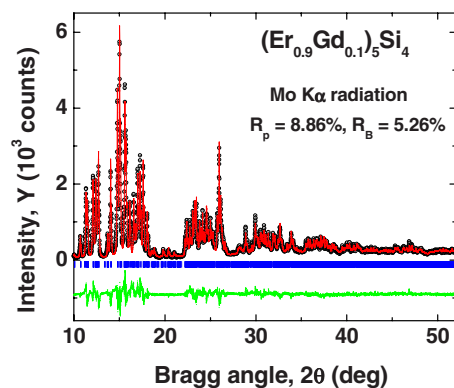

FIG. 1. (Color online) The observed (open circles) and calculated (lines through the open circles) powder diffraction patterns of $(Er_{0.9}Gd_{0.1})_5Si_4$ after the completion of the Rietveld refinement. The calculated positions of the Bragg peaks are shown as vertical bars just below the plots of the observed and calculated intensities. The differences between the observed and calculated intensities are shown at the bottom of the plot.

ence of a field and the $M(T)$ data were collected during the heating of the sample. The heating and cooling rates during all the ZFC, FCC, and FCW measurements were 3 K/min. All the ac measurements were obtained under ZFC condition. The magnetic relaxation measurements were carried out after cooling the samples from 200 K to the desired temperature under the ZFC conditions. After reaching the aimed temperature, a 1 kOe field was applied for 5 min and the time dependence of magnetization was measured immediately after the field was switched off. Some relaxation measurements were performed after the application of a 20 kOe field for 5 min and then reducing the field to zero for measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows a representative refined pattern of $(Er_{0.9}Gd_{0.1})_5Si_4$ collected using Mo $K\alpha$ radiation. The Rietveld refinement reveals that both the compounds crystallize in the Gd_5Si_4-type orthorhombic structure (O-I); however, the alloy with $x=0.25$ contains a small amount (<5 vol %) of the hexagonal R_5Si_3 compound. The lattice parameters a, b, and c of the compound with $x=0.1$ are 7.3080(3), 14.4134(5), and 7.6180(3) Å, respectively, whereas for the compound with $x=0.25$, the values of the lattice constants are 7.3254(5), 14.459(1), and 7.6412(5) Å, respectively. Using the reported room temperature lattice parameters of Er_5Si_4 (Ref. 22) and Gd_5Si_4,[31] the concentration dependence of a, b, and c of $(Er_{1-x}Gd_x)_5Si_4$ compounds is shown in Fig. 2. We note that the lattice parameters increase linearly with Gd concentration and the linear evolution of these parameters with substitution of larger sized Gd^{3+} ion is in accord with Vegard's law.

Figure 3 shows the temperature variation of the magnetization (M) of $(Er_{1-x}Gd_x)_5Si_4$ compounds with $x=0.1$ and 0.25 measured in the presence of an applied field (H_{dc}) of 1 kOe under ZFC, FCC, and FCW conditions. The insets show the temperature derivatives of the FCW data. Both Gd-
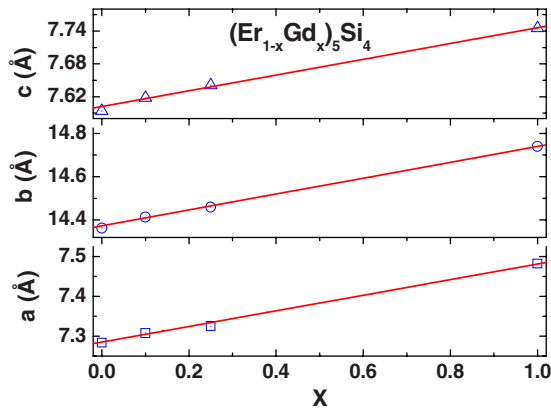
FIG. 2. (Color online) Concentration dependence of lattice parameters a, b, and c of (Er$_{1-x}$Gd$_x$)$_5$Si$_4$ compounds. The line through the data points shows the linear fit to the experimental data.

doped compounds show two prominent magnetic transitions and a weak anomaly at ~12 K [see insets in Figs. 3(a) and 3(b)]. Though the major magnetic transitions can be seen in M-T data measured under ZFC, FCC, and FCW conditions, the weak 12 K magnetic anomaly can clearly be seen only in the temperature derivatives of FCC [not shown in Fig. 3(a)] and FCW data but no signature of it was found in the derivatives of the ZFC data. The transitions seen at higher tempera-
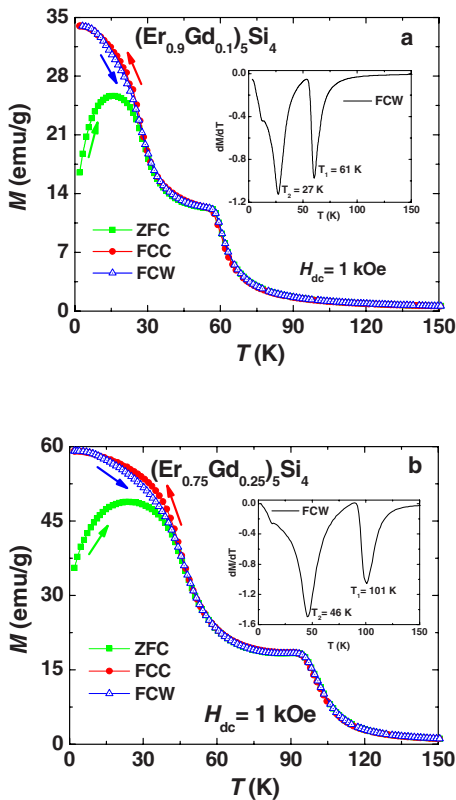

FIG. 3. (Color online) Temperature dependencies of the magnetization of (a) (Er$_{0.9}$Gd$_{0.1}$)$_5$Si$_4$ and (b) (Er$_{0.75}$Gd$_{0.25}$)$_5$Si$_4$ measured in an applied field (H_{dc}) of 1 kOe under ZFC, FCC, and FCW conditions. The insets show the temperature derivatives of the FCW data.
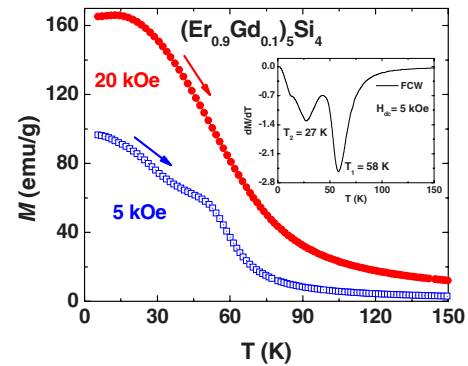

FIG. 4. (Color online) Temperature dependencies of the magnetization of (Er$_{0.9}$Gd$_{0.1}$)$_5$Si$_4$ measured in fields of 5 and 20 kOe under FCW condition. The inset shows the temperature derivative of the 5 kOe FCW data.

ture (T_1=61 K and 101 K for x=0.1 and 0.25, respectively) are antiferromagnetic like, whereas the ones seen at low temperature (T_2=27 K and 46 K for x=0.1 and 0.25, respectively) have ferromagnetic character. We note that Er$_5$Si$_3$ and Gd$_5$Si$_3$ order antiferromagnetically with Néel temperatures of 20 and 75 K, respectively.[32] However, the magnetization data of the compound with x=0.25 (i.e., the sample which has less than 5% R_5Si$_3$ impurity phase) do not show any anomaly in the vicinity of 20 or 75 K, thereby indicating that the presence of a small amount of these impurities does not affect bulk magnetization properties of (Er$_{0.75}$Gd$_{0.25}$)$_5$Si$_4$. Since both (Er$_{1-x}$Gd$_x$)$_5$Si$_4$ compounds show a weak magnetic anomaly around 12 K, it seems to be an intrinsic property of the investigated compounds and is likely indicative of some spin reorientation transition. A similar weak magnetization anomaly around 12 K has been reported in the Er$_5$Si$_4$ compound as well, and it has been attributed to a change in the magnetic structure at low temperatures in the magnetically ordered phase.[22,27]

Figure 4 shows the FCW $M(T)$ plots for (Er$_{0.9}$Gd$_{0.1}$)$_5$Si$_4$ collected under applied fields of 5 and 20 kOe. It may be noted that in a field of H_{dc}=5 kOe the transition associated with T_1 is pushed to a lower temperature (61 K for 1 kOe vs 58 K for 5 kOe). A similar result was obtained for (Er$_{0.75}$Gd$_{0.25}$)$_5$Si$_4$. At H_{dc}=20 kOe, the two transitions have merged into a broad minimum in the temperature derivatives of the FCW data: observed at about 53 and 92 K for the compounds with x=0.1 and 0.25, respectively. Therefore, the fact that a few kilo-oersted increment of the H_{dc} shifts the transition associated with T_1 to lower temperatures indicates that this magnetic transition is from the paramagnetic state to a magnetically ordered state with a complex noncollinear structure having an appreciable antiferromagnetic component; the ferromagneticlike transition at T_2 then leads to increasing collinearity of this magnetic structure. It may be mentioned here that the neutron diffraction studies by Cadogan et al.[24] have shown that orthorhombic Er$_5$Si$_4$ possesses a canted magnetic structure with ferromagnetic order along [010] and antiferromagnetic order in the perpendicular (010) plane. Associated with the presence of the antiferromagnetic component, a similar suppression of the magnetic

phase transition temperature has been reported in pure mono-clinic Er_5Si_4.[22]

Apart from the occurrence of multiple magnetic transitions, another feature worth noting in Fig. 3 is the large thermomagnetic irreversibility seen between the ZFC, FCC, and FCW $M(T)$ data. It is well known that the thermomagnetic irreversibility between the ZFC and FCC/FCW data is generally observed in magnetic materials with narrow domain walls or in materials having competing interactions.[33–36] In magnetic materials with narrow domain walls, under ZFC condition, the motion of the walls is hindered by pinning centers at low temperatures, thereby giving rise to a small magnetization. As the temperature is raised, thermal energy provides necessary driving force to overcome the barriers presented by the pinning centers, leading to an increase in the magnetization with increasing temperature. The increase in magnetization due to thermal activation of the domain walls is a likely reason for the absence of the magnetic anomaly at 12 K mentioned above. However, under the FCC/FCW, the magnetic field is applied in the paramagnetic regime, and therefore, the domain walls move in the direction of the field as the sample is cooled through the magnetic ordering temperature leading to high value of magnetization at low temperatures in the FCC/FCW conditions.[33,35] Owing to the low ordering temperature and relatively large magnetocrystalline anisotropy, which is seen in many compounds of the R_5T_4 family,[9,37–39] the title compounds may be considered as narrow domain wall systems, and therefore, the thermomagnetic irreversibility seen in Fig. 3 may, at least in part, be attributed to the pinning effects.

Considering that $M(T)$ data collected in different magnetic fields indicate the presence of both antiferromagnetic and ferromagnetic transitions, certain contribution from competing interactions in the thermomagnetic irreversibility may not be ruled out. As seen in Fig. 3, the FCC and FCW data show some irreversibility, especially for $x=0.25$. Generally, such irreversibility between the FCC and FCW data occurs in materials, exhibiting first order phase transitions. However, it is interesting to note that, opposite to many of the R_5T_4 compounds with first order transitions, the magnetization values during FCW are lower than those of FCC values. A similar behavior has been observed in other intermetallic compounds as well.[40]

Figure 5 shows the temperature dependence of the inverse dc susceptibility (H/M) of $(Er_{0.9}Gd_{0.1})_5Si_4$ obtained in applied field of 1 kOe and the Curie-Weiss $[H/M=C/(T-\Theta_P)]$ fit to the experimental data. The inset in the figure shows the same using 20 kOe $M(T)$ data. The arrows in the figure indicate the temperatures below which the deviations from the Curie-Weiss law are observed. Above 63 K, the inverse susceptibility measured in 1 kOe field obeys the Curie-Weiss law and, no deviation from this behavior is seen up to 300 K. This indicates that partial replacement of Er by Gd in Er_5Si_4 leads to the suppression of the structural transition seen in the parent compound.[20] The Curie-Weiss fit to the susceptibility data yields a paramagnetic Curie temperature (Θ_P) of 56 K and the effective moment (p_{eff}) of $9.3\mu_B/R^{3+}$. The expected p_{eff} for a mixture of $0.9Er+0.1Gd$ noninteracting trivalent ions is $9.4\mu_B/R^{3+}$. For
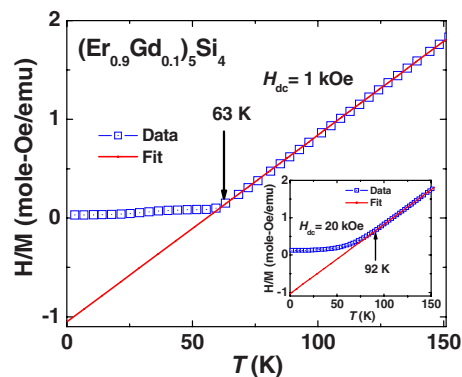

FIG. 5. (Color online) Temperature dependence of the inverse susceptibility (H/M) of $(Er_{0.9}Gd_{0.1})_5Si_4$ obtained under an applied field of (H_{dc}) 1 kOe. The line in the figure shows the Curie-Weiss fit to the experimental data. The inset shows the experimental H/M vs T data obtained in 20 kOe field along with the Curie-Weiss fit to it. The arrows indicate the temperature below which the deviation from the Curie-Weiss behavior starts.

$(Er_{0.75}Gd_{0.25})_5Si_4$, Θ_P and p_{eff} are 100 K and $9.1\mu_B/R^{3+}$, respectively, whereas the expected p_{eff} for a mixture of $0.75Er+0.25Gd$ is $9.2\mu_B/R^{3+}$. It should be mentioned here that although the $M(T)$ data of these compounds indicate the presence of both the antiferromagnetic and ferromagnetic transitions, the positive value of Θ_P is consistent with predominantly ferromagnetic interactions in the ground states for both of the compounds.

Another feature worth noticing in Fig. 5 is temperatures below which the magnetization no longer follows the Curie-Weiss behavior. In the field of 1 kOe, deviation from linearity begins at ~63 K, whereas for the 20 kOe field data, this deviation from the Curie-Weiss behavior starts at ~92 K. A similar behavior was observed in $(Er_{0.75}Gd_{0.25})_5Si_4$ as well. It is well known that intermetallic compounds with complex magnetic interactions may exhibit short range ferromagnetic correlations above their magnetic ordering temperature[41,42] and show a tendency to a saturation of the magnetization with field measured at temperatures above the ordering temperature. Therefore, in the title compounds, in high fields, the departure from the Curie-Weiss behavior at temperatures well above the zero field ordering temperature may be attributed to the presence of field induced short range ferromagnetic correlations.

To further understand the nature of the magnetic transitions seen in the $(Er_{1-x}Gd_x)_5Si_4$ compounds, we have also measured the temperature dependencies of the ac susceptibility. The real component of the ac susceptibility (χ') of $(Er_{0.75}Gd_{0.25})_5Si_4$ is shown in Fig. 6 as a representative plot. The temperature variation of the imaginary part of the ac susceptibility (χ'') is shown in the inset. Magnetic transitions are observed at ~97 K and 46 K, which compares well with the transition temperatures determined from the dc magnetization data. At temperatures above 100 K, the value of the χ'' is close to zero. However, χ'' increases below 100 K, and at ~95 K, a small peak in the $\chi''(T)$ plot is also seen. With further reduction in the temperature, the value of χ'' increases slowly up to ~46 K and then peaks at about 30 K,
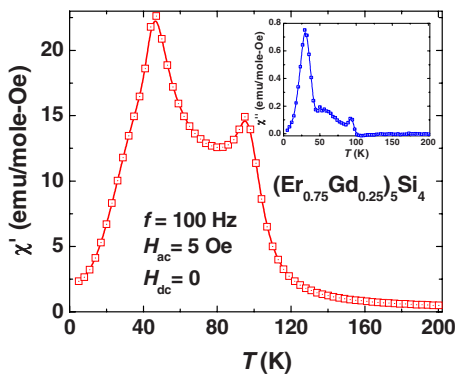
FIG. 6. (Color online) Temperature dependence of the real component of ac susceptibility (χ') of $(Er_{0.75}Gd_{0.25})_5Si_4$. The inset shows the temperature variation of the imaginary component of the ac susceptibility (χ'').

falling off rapidly below 30 K. It is well known that the nonzero value of χ'' is associated with energy loss processes. Usually, a peak in the $\chi''(T)$ plot is associated with either a ferromagnetic transition or a spin-glass phase. No such behavior is seen in antiferromagnets.[37,43] Therefore, in the present case, a nonzero value of χ'' seen at ~ 100 K along with results obtained from the temperature variation of dc magnetization in different fields indicates that although the magnetic transition associated with T_1 is predominantly antiferromagnetic in character, a certain level of ferromagnetism is also present at this temperature. These observations indicate that the magnetic ordering transition seen at T_1 is quite complex and presumably arises from a noncollinear magnetic structure. The rapid increase in the χ'' value below 46 K may be taken as an indication of bulk ferromagnetic ordering taking place at this temperature, which is consistent with the dc magnetization data. A similar behavior of the ac susceptibility is seen in $(Er_{0.9}Gd_{0.1})_5Si_4$ as well.

Figure 7 shows the $M(H)$ isotherm of $(Er_{0.75}Gd_{0.25})_5Si_4$ measured at 5 K. At low fields (up to ~ 5 kOe), the magnetization shows a fast increase, which is associated with the

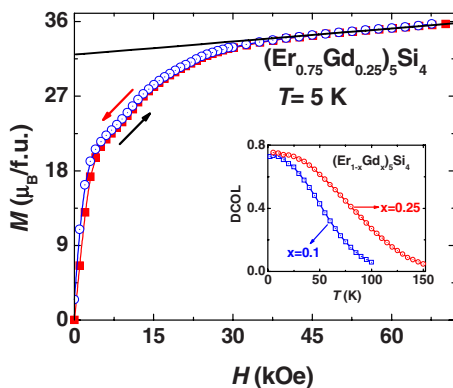FIG. 7. (Color online) Field dependence of magnetization of $(Er_{0.75}Gd_{0.25})_5Si_4$ at 5 K. The straight line in the figure shows the linear fit to the high field data. The inset shows the temperature variation of the degree of collinearity (DCOL) of the $(Er_{1-x}Gd_x)_5Si_4$ compounds.

displacement of the domain walls, a behavior typical for ferromagnets. With a further increase of the field, the magnetization increases rather slowly and shows a metamagneticlike transition in the field range of 10–15 kOe, which may be attributed to a change in the magnetic structure with the field. A similar broad metamagneticlike transition has been reported in Er_5Si_4.[25] At higher fields (above 35 kOe), the magnetization data show little to no tendency toward saturation and M varies linearly with field. At 5 K and $H = 70$ kOe, the values of the magnetization for $(Er_{0.9}Gd_{0.1})_5Si_4$ and $(Er_{0.75}Gd_{0.25})_5Si_4$ are found to be $7.34\mu_B/R^{3+}$ and $7.14\mu_B/R^{3+}$, respectively, whereas the expected saturation values of magnetization for both of these compounds are $8.8\mu_B/R^{3+}$ and $8.5\mu_B/R^{3+}$, respectively. The observed magnetization values in these compounds are significantly smaller than the expected saturation values, which may arise either due to the presence of antiferromagnetic correlations or due to a strong magnetocrystalline anisotropy. It may be mentioned here that, in general, the magnetic R_5T_4 materials with large anisotropy show considerable hysteresis and possess large value of remanence and coercivity.[44] However, the $(Er,Gd)_5Si_4$ compounds do not show a particularly large hysteresis. Furthermore, at 5 K, remanence magnetization and coercive field are low; for the compound with $x=0.1$, the remanence is ~ 20 emu/g and coercivity is ~ 500 Oe, whereas for the compound with $x=0.25$, these values are ~ 21 emu/g and ~ 380 Oe, respectively. Hence, the nonsaturation seen in both $(Er_{1-x}Gd_x)_5Si_4$ compounds arises from antiferromagnetic correlations, presumably also resulting in a noncollinear magnetic structure. It may be recalled here that the $M(T)$ data of these compounds also suggest a noncollinear magnetic structure.

Using the linear fit to the high field magnetization data (between 50 and 70 kOe) obtained at various temperatures and extrapolating it to zero field, degrees of collinearity (fractions of ferromagnetism) as well as their temperature dependencies have been estimated. Under the assumption that the nonsaturation behavior seen in the $(Er_{1-x}Gd_x)_5Si_4$ compounds results from a complex noncollinear magnetic structure, the ferromagnetic fraction reflects the extent to which the moments can be aligned to the direction of the applied field. Therefore, we call the ferromagnetic fraction of the $(Er_{1-x}Gd_x)_5Si_4$ compounds, normalized to their respective expected moments ($8.8\mu_B/R^{3+}$ and $8.5\mu_B/R^{3+}$ for $x=0.1$ and 0.25, respectively), the degree of collinearity (DCOL). Temperature variations of the degree of collinearity are shown as inset of Fig. 7. In both compounds at low temperatures, the DCOL is more than 75%; however, their temperature dependencies are different. It is also worth noting that both compounds posses considerable DCOL at temperatures well above their zero field ordering temperatures. Furthermore, even though the low field $M(T)$ data for these compounds show the presence of two magnetic transitions, the DCOL vs T plots do not show these anomalies. Considering that the ferromagnetic fraction and, therefore, the DCOL have been calculated from the extrapolation of the high field M-H data to the zero field, the temperature variation of the degree of collinearity effectively reflects the $M(T)$ data collected in high fields. In general, the magnetic transitions get broad-
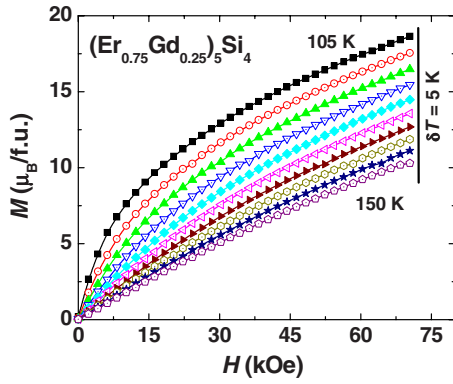
FIG. 8. (Color online) The $M(H)$ isotherms of $(Er_{0.75}Gd_{0.25})_5Si_4$ measured above its ordering temperature ($T_1 = 101$ K).

ened in high fields and hence the absence of anomalies corresponding to T_1 and T_2 in DCOL vs T plots is expected. This observation is consistent with the presence of a broad transition in the M-T data collected in 20 kOe.

Figure 8 shows the $M(H)$ isotherms of $(Er_{0.75}Gd_{0.25})_5Si_4$ measured above its upper ordering temperature ($T_1 = 101$ K). These $M(H)$ curves show a strong curvature at low fields and no tendency to saturation in high fields. Such a strong curvature in the $M(H)$ isotherms well above the ordering temperature has been observed in other intermetallics also[34,42] and is usually attributed to the presence of short range ferromagnetic correlations above T_C. It is worth mentioning here that for the calculation of the degree of collinearity in the title compounds, the straight lines were fitted in the field range of 50–70 kOe and therefore the presence of these short range ferromagnetic correlations seem to be responsible for considerable degree of collinearity at temperatures above the ordering temperatures of these compounds (see inset of Fig. 7).

In order to further understand the magnetic properties of these compounds, we have also measured the temperature variation of the heat capacity (C), and Fig. 9(a) shows the $C(T)$ plot for $(Er_{0.75}Gd_{0.25})_5Si_4$ as a representative. The temperature dependence of the magnetic contribution to the heat capacity (C_{mag}) of $(Er_{0.75}Gd_{0.25})_5Si_4$ is shown in Fig. 9(b). Following Gschneidner et al.,[45] the nonmagnetic contributions to the heat capacity, i.e., the lattice plus the electronic contributions, of the title compounds have been estimated by taking the appropriate prorated heat capacities of La_5Si_4 and Lu_5Si_4 to mimic the particular $(Er_{1-x}Gd_x)_5Si_4$ compounds. For the compound with $x = 0.1$, the nonmagnetic contribution to the heat capacity was approximated by 24% La_5Si_4 + 76% of Lu_5Si_4, whereas for the compounds with $x = 0.25$, it was approximated by 28% La_5Si_4 + 72% of Lu_5Si_4. It may be noted from Fig. 9(a) that $C(T)$ data show a λ-type anomaly peaking at 98 K which is consistent with the magnetic transition seen in the $M(T)$ data at T_1 ($T_1 \sim 101$ K). The low temperature magnetic transition seen at T_2 ($T_2 \sim 46$ K) in the $M(T)$ data is manifested by a shoulder in the zero field $C(T)$ data. The occurrence of the magnetic transitions is more clearly observed in the C_{mag} vs T plot [Fig. 9(b)]. At low temperatures, the C_{mag} increases rapidly with temperature
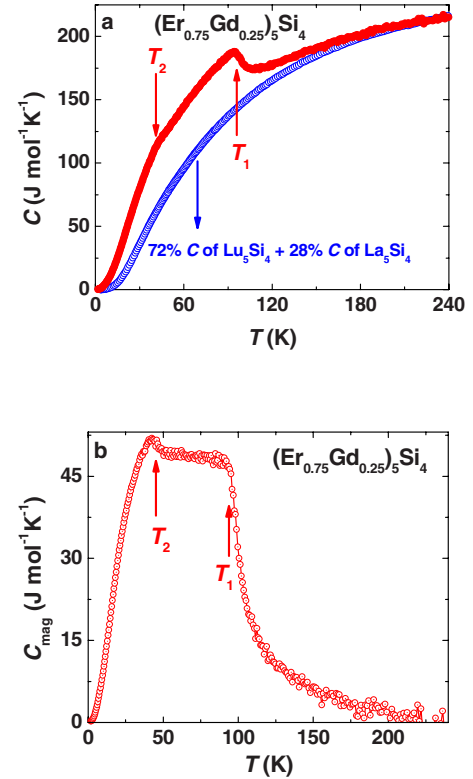

FIG. 9. (Color online) Temperature dependence of (a) heat capacity (C) of $(Er_{0.75}Gd_{0.25})_5Si_4$ along with the prorated heat capacities of La_5Si_4 and Lu_5Si_4 to mimic the nonmagnetic contributions to the heat capacity and (b) temperature variation of the magnetic contribution to heat capacity (C_{mag}).

and peaks around 44 K. Between 50 and 95 K, C_{mag} remains fairly constant, and around 100 K, a rapid drop in C_{mag} is observed. At ~ 44 K, the peak seen in the C_{mag} vs T plot characterizes the low temperature magnetic transition observed at T_2, whereas the rapid drop corresponds to order-disorder magnetic transition seen at T_1 (also see Fig. 3). It may also be noted that though the C_{mag} drops rapidly above T_1, its magnitude remains considerable at temperatures well above T_1. Such a magnetic precursor effect in the temperature variation of C_{mag} has been reported in other intermetallic compounds also and is expected to arise either from to the presence of short range ferromagnetic correlations or from spin fluctuations above the ordering temperature.[41,46] As noted earlier, the low field inverse susceptibility of the title compounds (see Fig. 5) obeys Curie-Weiss law down to temperatures close to the magnetic ordering temperature and hence negate the presence of short range ferromagnetic correlation in paramagnetic state in small fields. Therefore, the considerable C_{mag} at temperatures well above the ordering temperatures in the title compounds is attributed to spin fluctuations. Similar behavior in the temperature dependence of C_{mag} is also seen for $(Er_{0.9}Gd_{0.1})_5Si_4$. Using the temperature dependencies of C_{mag}, magnetic entropy of the title compounds has also been calculated. For $(Er_{0.9}Gd_{0.1})_5Si_4$ and $(Er_{0.75}Gd_{0.25})_5Si_4$, the calculated magnetic entropies are found to be 103 and 97 J mol^{-1} K^{-1}, respectively, whereas the theoretically expected magnetic entropies, i.e., the
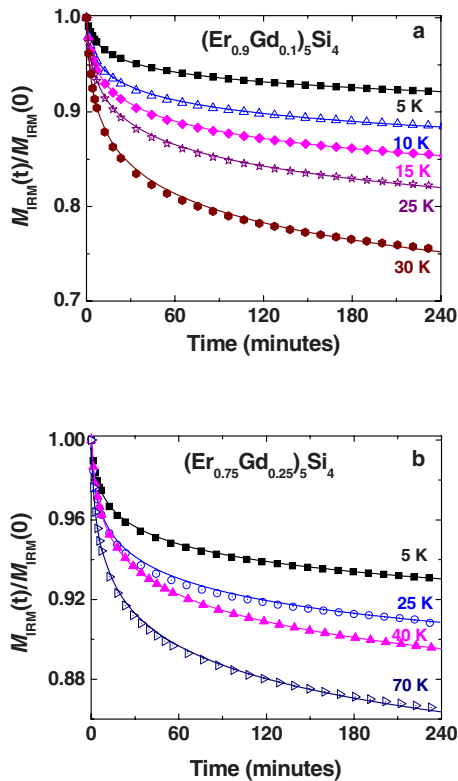
FIG. 10. (Color online) Time (t) dependencies of the isothermal remanent magnetization $[M_{IRM}(T,t)]$ normalized to the value at $t = 0$ $[M_{IRM}(T,0)]$ of (a) $(Er_{0.9}Gd_{0.1})_5Si_4$ and (b) $(Er_{0.75}Gd_{0.25})_5Si_4$. The open symbols represent the experimental data points, whereas the lines through them are fits of the equation $M_{IRM}(T,t) = M_{IRM}(T,0) - S(T)\ln(1+t)$.

$R\ln(2J+1)$ values for these compounds are 112 and 110 J mol^{-1} K^{-1}, respectively.

It was mentioned above that $M(T)$ in these compounds shows irreversible behavior between the FCC and FCW data, i.e., the FCW curves lie below the FCC data. Recently, Nirmala *et al.*[40] have reported that such irreversibility between the FCC and FCW data may also arise due intrinsic frustration associated with the spin system. In order to understand the role of complex magnetic interactions on the stability of the zero field magnetic state, we carried out relaxation measurements on these compounds and the results are shown in Fig. 10. The isothermal remanent magnetization (M_{IRM}) of $(Er_{1-x}Gd_x)_5Si_4$ compounds shows strong time dependence and there is no saturation even after 240 min. The relaxation behavior could be fitted to the following equation:

$$M_{IRM}(T,t) = M_{IRM}(T,0) - S(T)\ln(1+t), \quad (1)$$

where $M_{IRM}(T,0)$ and $S(T)$ are initial zero field remanent magnetization and magnetic viscosity, respectively. The $M_{IRM}(T,0)$ and $S(T)$ values obtained from the fit of the above equation to the relaxation data collected at various temperatures are given in Table I. With increasing temperature, both $M_{IRM}(T,0)$ and $S(T)$ decrease, which is consistent with previous reports on other intermetallic compounds.[47] Logarithmic time dependence of the isothermal remanent

TABLE I. The value of initial zero field remanent magnetization $[M_{IRM}(T,0)]$ and magnetic viscosity for $(Er_{1-x}Gd_x)_5Si_4$ compounds at various temperatures.

Compound	T (K)	$M_{IRM}(T,0)$ (emu/g)	$S(T)$ (emu/g)
$(Er_{0.9}Gd_{0.1})_5Si_4$	5	8.361	0.132
	10	6.200	0.128
	15	4.852	0.125
	20	3.591	0.117
	25	2.199	0.073
	30	0.727	0.033
$(Er_{0.9}Gd_{0.1})_5Si_4$	5	9.421	0.120
	25	4.098	0.066
	40	2.929	0.057
	70	0.586	0.014

magnetization data has been observed in many other intermetallic compounds[48,49] and, in general, such an M_{IRM} vs t dependence is characteristic of magnetic materials with hysteretic magnetization or of spin glasses.[50,51] As a general rule, materials with high coercivity show a pronounced time dependent behavior; however, if the applied field is higher than the coercive field, the observed relaxation is attributed to the spin glass behavior.[47,51] We recall here that at 5 K, the coercive fields for $(Er_{1-x}Gd_x)_5Si_4$ compounds with $x=0.1$ and 0.25 are 500 and 380 Oe, respectively, and the relaxation measurements were performed after the application of 1 kOe, which is much higher compared to the coercive fields seen in these compounds. Therefore, the above observation and the fact that the relaxation data collected after the application of a 20 kOe field (not shown in Fig. 10) are similar point toward a microscopic (spins) rather than macroscopic (domains) origin of this behavior.

Representative plots of the ac susceptibility data measured at various frequencies for $(Er_{0.9}Gd_{0.1})_5Si_4$ are shown in Fig. 11. Similar plots were obtained for the compound $(Er_{0.75}Gd_{0.25})_5Si_4$ as well. It is well known that for spin glasses, the magnitude of the real part of the ac susceptibility and the position of the peaks seen in the χ' vs T curve
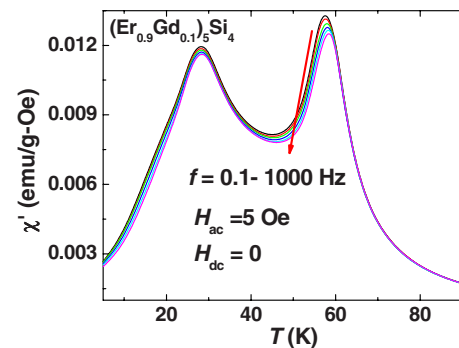

FIG. 11. (Color online) Temperature dependencies of the real component of the ac susceptibility (χ') of $(Er_{0.9}Gd_{0.1})_5Si_4$ collected at 0.1, 0.5, 1, 10, 100, and 1000 Hz frequencies (f).

strongly depend on frequency (f) of the ac field.[43,50] However, as follows from Fig. 11, χ' of $(Er_{0.9}Gd_{0.1})_5Si_4$ shows only a weak frequency dependence. A typical frequency shift (δT_m) calculated as $\delta T_m = \Delta T_m/(T_m \Delta \log f)$, where T_m is the temperature at which a peak in χ' vs T appears and ΔT_m is the increment in the peak position by the frequency, for metallic spin glass systems have been reported to be ~0.01.[49,52] In $(Er_{0.9}Gd_{0.1})_5Si_4$, the peak at high temperature (T_1) in the χ' vs T weakly depends on the frequency, whereas the one associated with low temperature (T_2) is frequency independent. The observed frequency shift associated with the transition at T_1 is 0.004, which is nearly an order of magnitude smaller than the typical frequency shift seen in metallic spin glasses.[49,52] For $(Er_{075}Gd_{0.25})_5Si_4$, both the peaks at T_1 and T_2 are found to be practically frequency independent. Therefore, the presence of a spin glass state in these compounds can be ruled out; though the strong relaxations seen in the isothermal remanent magnetization (see Fig. 10) point toward a spin-glass-like magnetic state. At this point, it is worth mentioning that such a strong relaxation in the magnetization without (or with a weak) frequency dependence in the χ' vs T data has been reported in some other intermetallics with long range magnetic order[47,49] and, therefore, the interpretation of the magnetic relaxation data in terms of spin glass behavior should be done with caution. We recall here that the $M(T)$ and $M(H)$ data of the title compounds indicate complex magnetic state with ferromagnetic as well as antiferromagnetic correlations, and therefore, considerable magnetic relaxation seen here is likely a consequence it. The opposite trend between irreversibility in FCC and FCW data, i.e., FCW being less than FCC (see Fig. 3) is a result of the intrinsic frustration arising from a complexity and anisotropy of the indirect exchange in these layered and distinctly anisotropic systems. Associated with the intrinsic frustration, a similar unconventional irreversibility between FCC and FCW data has been reported in $(Er_{0.75}Dy_{0.25})Al_2$ as well.[40]

Figures 12(a) and 12(b) show the temperature variation of the MCE, calculated in terms of the isothermal magnetic entropy change for various field changes (ΔH) of $(Er_{1-x}Gd_x)_5Si_4$ compounds with $x=0.1$ and 0.25, respectively. The ΔS_M vs T plots for these compounds have been obtained from the $M(H)$ data collected at various temperatures and employing Maxwell's relation.[4] The ΔS_M vs T plots for both the compounds peak near their ordering temperature and the peak position remains same for all ΔH between 10 and 70 kOe. Both compounds exhibit positive MCE (negative ΔS_M), which corroborates the presence of large ferromagnetic fractions or degrees of collinearity (see inset of Fig. 7) in these compounds. A small negative MCE seen at low temperatures (below 10 K) is a consequence of hysteretic effects.

Corresponding to the various field changes, the maximum values of ΔS_M (ΔS_M^{max}) for the $(Er_{1-x}Gd_x)_5Si_4$ compounds are given in Table II. The MCE of $(Er_{0.9}Gd_{0.1})_5Si_4$ is almost equal to that of pure Er_5Si_4,[22] but the MCE of $(Er_{0.75}Gd_{0.25})_5Si_4$ is lower. We note that, because of the larger de Gennes factor of Gd (15.75 for Gd vs 2.55 for Er),[53] the partial replacement of Er by Gd in Er_5Si_4 is expected to enhance the ordering temperature [indeed seen from the
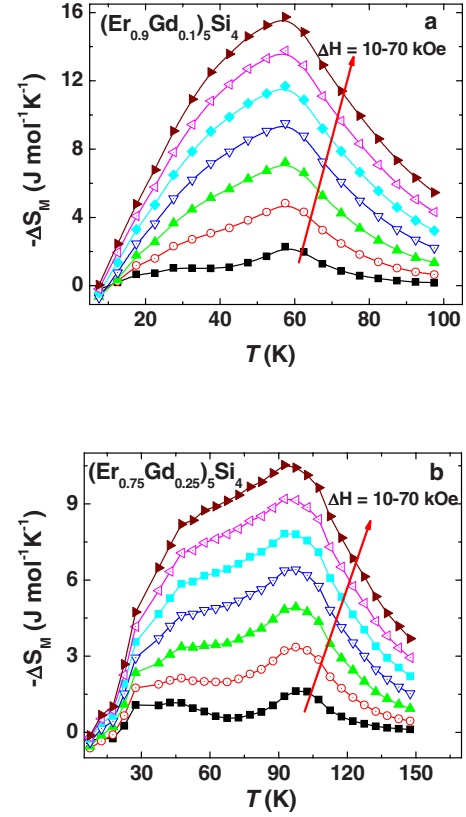

FIG. 12. (Color online) Temperature dependencies of isothermal magnetic entropy change (ΔS_M) of $(Er_{1-x}Gd_x)_5Si_4$ as calculated from magnetization data for (a) $x=0.1$ and (b) $x=0.25$, obtained for various field changes (ΔH).

$M(T)$ data], and would lead to a reduction in the total available magnetic entropy [$R\ln(2J+1)$: 17.29 J mol^{-1} K^{-1} for Gd vs 23.05 J mol^{-1} K^{-1} for Er]. Furthermore, it is well known that, in general, the increase in the thermal load resulting from the increase in ordering temperature diminishes the ΔS_M (Ref. 4), and therefore, the replacement of Er by Gd in the Er_5Si_4 is expected to reduce the ΔS_M^{max} values. However, the fact that ΔS_M^{max} for $(Er_{0.9}Gd_{0.1})_5Si_4$ is almost equal to that of Er_5Si_4 (see Table II), even though its ordering temperature is nearly doubled, suggests that the magnetocaloric properties of Er_5Si_4 are enhanced by small Gd substitutions. This may be attributed to the reduction in anisotropy of Er_5Si_4 brought about by the Gd substitution. The reduction

TABLE II. The maximum value of isothermal entropy change (ΔS_M^{max}) of $(Er_{1-x}Gd_x)_5Si_4$ compounds for various field changes (ΔH). The data for the compound $x=0$ have been taken from Ref. 22.

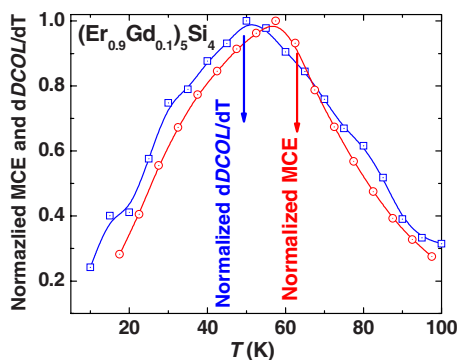| ΔS_M^{max} (J mol^{-1} K^{-1}) $x=0$	ΔS_M^{max} (J mol^{-1} K^{-1}) $x=0.1$	ΔS_M^{max} (J mol^{-1} K^{-1}) $x=0.25$	ΔH (kOe)
4.9	4.8	3.2	20
11.7	11.7	7.8	50
	15.7	10.5	70

FIG. 13. (Color online) Temperature dependence of MCE and derivative of the degree of collinearity (dDCOL/dT) of $(\mathrm{Er}_{0.9}\mathrm{Gd}_{0.1})_5\mathrm{Si}_4$ normalized to their maximum values.

seen in the $\Delta S_M^{\mathrm{max}}$ value of $(\mathrm{Er}_{0.75}\mathrm{Gd}_{0.25})_5\mathrm{Si}_4$ is consistent with the reduction in the total magnetic entropy and increase in the ordering temperature. We note that maximum volumetric magnetic entropy change for the potential magnetic refrigerants such as $(R,R')\mathrm{Al}_2$ compounds with ordering temperature between 50 and 100 K lies between $\sim$110 and 60 mJ cm^{-3} K^{-1}.[4] For $(\mathrm{Er}_{1-x}\mathrm{Gd}_x)_5\mathrm{Si}_4$ compounds with x =0.1 and 0.25, the maximum volumetric magnetic entropy changes are $\sim$97 and 65 mJ cm^{-3} K^{-1}, respectively. Therefore, a comparison of the volumetric magnetic entropy change of the title compounds with those of the $(R,R')\mathrm{Al}_2$ indicates that $(\mathrm{Er}_{1-x}\mathrm{Gd}_x)_5\mathrm{Si}_4$ compounds may be useful for magnetic refrigeration application in the cryogenic temperature regime. Another feature worth noting in Fig. 12 is the occurrence of a considerable MCE at temperatures well above the ordering temperatures of these compounds. A similar behavior has been reported in the temperature variation of the MCE of HoNiAl also[34] and may be attributed to the presence of field induced short range ferromagnetic correlations in these compounds.

Figure 13 shows the temperature dependence of the MCE and the temperature derivative of the degree of collinearity (dDCOL/dT) of $(\mathrm{Er}_{0.9}\mathrm{Gd}_{0.1})_5\mathrm{Si}_4$, normalized to their maximum values. A similar plot was obtained for $(\mathrm{Er}_{0.75}\mathrm{Gd}_{0.25})_5\mathrm{Si}_4$ as well. Clearly, the normalized MCE and dDCOL/dT exhibit similar temperature variation, indicating a strong correlation between the MCE and dDCOL/dT. This is to be expected since ferromagnetic fraction or DCOL reflects the extent to which the moments can be aligned in the direction of the field. A similar correspondence between the MCE and ferromagnetic fraction has been reported in some manganites.[11] It may also be mentioned here that the main contribution to the degree of collinearity at temperatures above T_1 arises from the presence of field induced short range ferromagnetic correlations, and therefore, the similarity in dDCOL/dT and MCE indicates that short range correlations play an important role in deciding the magnetic and magnetothermal properties in these compounds.

IV. SUMMARY AND CONCLUSIONS

In conclusion, partial replacement of Er by Gd in $\mathrm{Er}_5\mathrm{Si}_4$ leads to the suppression of the structural transition seen in the parent compound and gives rise to the presence of both ferromagnetic and antiferromagnetic correlations. The existence of complex magnetic interactions lead to the formation of field induced short range ferromagnetic correlations which greatly affect the magnetization behavior in the paramagnetic state. The magnetization data of these compounds show strong relaxation with logarithmic time dependence. However, the frequency dependence of the ac susceptibility is negligible or very small and thus the observed magnetic behaviors are not due to the spin-glass formation in the $(\mathrm{Er}_{1-x}\mathrm{Gd}_x)_5\mathrm{Si}_4$ alloys. We believe that this behavior is due to the intrinsic frustration arising from the complex magnetic state arising from anisotropy of exchange interactions in these distinctly layered systems. Small replacements of Er by Gd in $\mathrm{Er}_5\mathrm{Si}_4$ improve magnetocaloric properties of the latter.

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