Observation of Griffiths-like phase in the quaternary Heusler compound NiFeTiSn

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Abstract

The quaternary Heusler compound NiFeTiSn can be considered to be derived from the exotic pseudogap-compound Fe₂TiSn by the replacement of one Fe atom by Ni. In contrast to Fe₂TiSn, which shows a disorder induced ferromagnetic phase, the ground state of NiFeTiSn is antiferromagnetic with the signature of spin canting. Interestingly, NiFeTiSn shows a Griffiths-like phase characterized by isolated ferromagnetic clusters before attaining the antiferromagnetic state. The Griffiths-like phase is possibly associated with the antisite disorder between Fe and Ti sites as evident from our powder x-ray diffraction study. The compound also shows rather unusual temperature dependence of resistivity, which can be accounted by the prevailing structural disorder in the system. NiFeTiSn turned out to be a rare example where Griffiths-like phase is observed in a semiconducting 3d transition metal based intermetallic compound with antiferromagnetic ground state.

Keywords: quaternary Heusler compound, Griffiths phase, antisite disorder

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent times, transition metal based Heusler compounds and alloys [1] are in the limelight of active research by virtue of their diverse and novel electronic properties, which include half-metallic ferromagnetism, spin-gapless semiconductivity, Weyl semimetallicity, magnetic shape memory effect, high Seebeck effect, magneto- and baro-caloric effects, unconventional superconductivity, anomalous Hall effect and so on [2–4]. Among others, Fe₂TiSn deserves a special mention in the Heusler family due to its fascinating electronic and magnetic properties. First principle density functional theory (DFT) based calculation indicates the compound to have a non-magnetic ground state with a pseudogap at the Fermi level ($E_F$) [5]. The number of valence electrons ($Z_v$) is 24 in Fe₂TiSn, which implies zero moment according to the Slater–Pauling rule [6]. However, actual experimental measurement indicates that the compound is a weak ferromagnet with Curie temperature ($T_C$) close to 260 K and saturation moment 0.2 $\mu_B$/f.u. [7]. The possible origin of ferromagnetism is ascribed to the antisite disorder between Fe and Ti sites, a phenomenon which is very common among Heusler compositions. Initial analysis of the low-temperature heat capacity and the resistivity data led to the conclusion that the compound was a heavy fermion [5]. Optical conductivity measurements, however, shows a simple Drude-like response of free carriers ruling out the Kondo or heavy fermion like state [5, 8]. The low temperature anomaly in Fe₂TiSn is believed to arise from clustering of atoms, which is also in accordance with the picture of disorder induced ferromagnetism in the system. Notably, the compound also shows large positive Seebeck coefficient at room temperature.

Fully ordered Fe₂TiSn crystallizes in the cubic L₂₁ structure with space group $Fm\bar{3}m$, where Fe atoms occupy 8c (1/4, 1/4, 1/4) Wyckoff position. In case of an L₂₁ full Heusler
compound with general formula $X_2YZ$, the replacement of one $X$ atom with a different transition metal ($X'$) leads to a change in structural symmetry. The resultant compound ($XX'YZ$) retains the cubic symmetry but attains a different space group, $F43m$. The study of such quaternary Heusler compounds have accelerated drastically in last two decades because of their possible application as a spin-polarized material in spintronics, such as CoFeMnSi, CoFeCrGa [13,14], Apart from their half metallic character, some of the quaternary compounds, such as CoFeMnSi, CoFeCrGa [13,14], are found to be spin-gapless-semiconductors.

Considering rich physics associated with the full Heusler Fe$_2$TiSn, it might be tempting to study the quaternary Heusler compound derived from it. There are previous reports on doping at the Fe site, however, a detailed study on the quaternary derivative is lacking. It is already known that Ni$_2$TiSn is a Pauli paramagnet with vanishing local moment at the Ni site [15]. Therefore, it is worth studying the quaternary compound NiFeTiSn, where one Fe site is diluted by a Ni atom. Such substitution will not only reduce the Fe concentration, it will also change the local crystallographic environment of Fe due to the change in space group.

The degree of antisite disorder depends on the atomic radii of the constituent metals, and it is likely to differ in case of NiFeTiSn. In the previous work on Fe$_{2-x}$M$_x$TiSn ($M = $ Ni, Co), superparamagnetic-like state has been predicted [16]. Also, doping is found to destroy the pseudogap at the $E_F$. Our present study on NiFeTiSn indicates an antiferromagnetic (AFM)-like state at very low temperature (below about 7 K), which is in sharp contrast with the ferromagnetic (FM) state reported for Fe$_2$TiSn. None less, NiFeTiSn shows a non-Curie–Weiss-like state below about 275 K indicating the presence of short range magnetic correlations. Our investigations suggest that this state with short range magnetic correlations complies with the properties of the Griffiths phase (GP). In GP, the magnetic correlation does not vanish immediately above the long range ordering temperature, but it continues to exist up to a higher temperature [17–21]. In systems having ordered magnetic ground state, GP occurs due to the percolative nature of the distribution of short-range FM clusters developed much above the ordering temperature in the magnetically disordered paramagnetic (PM) regime.

Magnetic materials, in presence of certain degree of disorder, can give rise to this remarkable GP-like magnetic state. In majority of the cases, the GP is followed by a long range FM order at low temperature. The occurrence of GP in the AFM compounds are mostly reported in pnictides, manganites, perovskites [22–27] and few other rare-earth intermetallic alloys [28,30,31]. On the contrary, NiFeTiSn is a transition metal based intermetallic system with rather simple cubic structure. Our careful investigation and analyses indicate that the ground state of NiFeTiSn can better be described by a canted AFM one. In addition, the compound shows negative temperature coefficient of resistivity with rather unusual temperature dependence.

2. Experimental details

Polycrystalline NiFeTiSn was prepared using the stoichiometric ratio of the constituent elements by arc melting procedure in an inert argon atmosphere followed by annealing at 800 °C for 3 days. Powder $x$-ray diffraction (PXRD) was performed at room temperature and the crystallographic structure was analysed using the Rietveld refinement technique with MAUD software package [32]. Magnetic measurements were carried out with the help of a commercial Quantum Design SQUID-VSM. The resistivity ($\rho$) was measured on a cryogen-free high magnetic field system (Cryogenic Ltd, UK) between 5–300 K. Thermoelectric measurements were carried out in the temperature range of 10 K–300 K using the differential technique. Heat capacity was measured using a Quantum Design physical properties measurement system.

To confirm the chemical composition of the sample, we performed a semi-quantitative energy dispersive $x$-ray (EDX) analysis over multiple areas of the samples, and the average composition from the EDX analysis is found to be Ni$_{25.1}$Fe$_{23.6}$Ti$_{24.8}$Sn$_{26.6}$. From the obtained value, the equiatomic quaternary compound can be considered to be stoichiometric within the accuracy (2%–5% [33]) of the EDX technique. $^{57}$Fe Mössbauer spectra were recorded using an alternating constant WissEl Mössbauer spectrometer. The system operates in a horizontal transmission geometry with source, absorber and detector in a linear arrangement. Isomer shifts were measured with reference to $\alpha$-iron metal foil at the same temperatures. Normos-A Mössbauer Fit programme was used to fit the experimental data.

3. Results

3.1. Powder $x$-ray diffraction

Room temperature PXRD pattern for the compound NiFeTiSn is shown in figure 1(a). From the observed reflections and subsequent refinements, the sample is found to crystallize in the cubic Y-II type structure without any impurity phases. In this structure, Ni, Fe, Ti and Sn occupy the lattice sites $4b(1/2,1/2,1/2)$, $4d(3/4,3/4,3/4)$, $4c(1/4,1/4,1/4)$ and $4a(0,0,0)$ respectively [34,35]. Both the superlattice reflection (111) and (200) are found to be present, indicating a predominantly ordered structure. For an ideal Y-type structure, the intensity of (111) and (200) in general remains the same. The reduction of (200) peak intensity in comparison to (111) peak ($I_{111}/I_{200} \sim 1.7$) might be due to the existence of antisite disorder in the studied sample. The cubic lattice parameter obtained from the refinement is found to be 6.070 Å.

It is important to obtain a quantitative idea of the degree of disorder from the intensities of the diffraction peaks. A rough estimation of the degree of site ordering of the constituent atoms can be made by calculating the quantities $p = I_{330}/I_{220}$ and $q = I_{111}/I_{220}$, where $I_{330}$ is the intensity of the (hkl) line in the PXRD pattern. The order parameters, $\sigma$ and $\alpha$ are given by,
Figure 1. (a) Shows the powder x-ray diffraction pattern of NiFeTiSn (data points) at room temperature using Cu Kα radiation. The solid line is the Rietveld refinement fit to the data. (b) Shows the Mössbauer spectrum of NiFeTiSn recorded at room temperature. The 80 K spectrum is shown in the inset.

\[ \sigma^2 = \frac{q_{\text{obs}}}{q_{\text{fit}}} \text{ and } \sigma^2(1 - 2\alpha)^2 = \frac{p_{\text{obs}}}{p_{\text{fit}}} \] [11]. Here the subscripts obs and fit correspond to the experimentally observed and the fitted values respectively. The fitted intensities are obtained from the Rietveld refinement without considering any site disorder. For an ideally ordered system, \( \sigma = 1 \) and \( \alpha = 0 \), and for fully B2 disordered case, \( \sigma = 1 \) and \( \alpha = 0.5 \). We get, \( \sigma = 1.08 \) and \( \alpha = 0.1 \) for NiFeTiSn. This indicates the presence of disorder (Fe–Ti antisite disorder) in case of NiFeTiSn.

Mössbauer spectra for NiFeTiSn (see figure 1(b)) recorded at both 300 K and 80 K exhibit singlet pattern, which indicates that local electric field at Fe site in the compound is symmetric. These singlet Mössbauer peaks at 300 and 80 K are well fitted with single Lorentzian function [36]. The isomer shift is also found to be slightly higher at low temperature [0.24 mm s\(^{-1}\) (300 K) and 0.28 mm s\(^{-1}\) (80 K)].

3.2. Magnetisation

Temperature (T) variation of magnetisation (M) recorded for zero-field-cooled (ZFC), field-cooled (FC) and field-cooled heating (FCH) conditions under the magnetic fields, \( H = 100 \) Oe and \( H = 1 \) kOe are shown in figures 2(a) and (c). Both ZFC and FC data are characterized by a peak around 7 K indicating an AFM-like transition (see figure 2(b)). More accurate value of the Néel temperature is obtained from the minimum of \( dM/dT \) versus T data, which is \( T_N = 11 \) K. ZFC and FC curves are found to bifurcate from each other from around \( T_{\text{irr}} = 270 \) K, which is much higher than \( T_N \). There is a broad shoulder occurring around 250 K, and on further cooling, M increases with T. This thermo-magnetic irreversibility well above \( T_N \) and the presence of broad shoulder-like feature hint towards the existence of the short-range magnetic correlations in the backdrop of a PM phase [37]. Under \( H = 1 \) kOe, the low-T bifurcation between ZFC and FC curves becomes weak and shifts to lower-T and the \( T_{\text{irr}} \) almost vanishes.
The downward behaviour of $\chi$ spontaneous magnetisation ($\text{sample recorded at different temperatures. Inset: variation of}$ $\chi$ of $\theta$ below about 300 K for the 100 Oe data (inset of figure 4(a)). A strong downward deviation from the CW law is observed from 100 and 50 K isotherms in figure 2(d)) reaffirms the existence of the short-range correlations. Inset of figure 2(d) shows an enlarged view of $M(H)$ at $T = 2$ K recorded in ZFC and FC conditions under $H = 250$ Oe, indicating small coercive field close to 200 Oe and the absence of any exchange-bias in the compound.

Figure 3 shows the Arrot ($M^2$ versus $H/M$) plot at few constant temperatures [38]. The curves are quasi-linear at higher values of $H/M$ for all temperatures above and below $T_N$. The linear extrapolation of the high-$H$ data shows positive intercept on the $M^2$ axis for the isotherms recorded below $T_N$. Such positive values of $M^2$ (below $T_N$), indicates the presence of spontaneous magnetisation, $M_s$ (as obtained from the square root of $M^2$). However, such positive intercept is absent for the data recorded above $T_N$. This indicates that there exists a finite $M_s$ only below $T_N$, and possibly the system has a canted AFM ground state.

In the main panel of figure 4(a), we have plotted inverse susceptibility ($\chi^{-1} = H/M$) as a function of $T$. A linear region is observed between 310–360 K, and we have fitted this part using the Curie–Weiss (CW) law, $\chi = C/(T - \theta_p)$, where $C$ is the Curie constant, $\theta_p$ is the PM CW temperature. From the fitting, we obtain the effective PM moment, $\mu_{\text{eff}}$ to be 2.48 $\mu_B$, and $\theta_p = 128$ K. The observed large positive value of $\theta_p$ indicates the presence of dominant FM correlations in the system.

To shed some light on the observed behaviour, we have plotted $\chi^{-1}$ versus $T$ data over a wide range of temperatures. A strong downward deviation from the CW law is observed from below about 300 K for the 100 Oe data (inset of figure 4(a)). This downward behaviour of $\chi^{-1}$ decreases with increasing $H$ and disappears for $H = 10$ kOe (figure 4(b)). The observation of a downward deviation in the $\chi^{-1}$ versus $T$ curve at temperatures much higher than magnetic ordering temperature (in this case $T_N$) is a hallmark of the presence of the Griffiths-like phase [37, 39, 40]. The GP is characterized by the appearance of the finite size FM clusters in the backdrop of a PM phase well above the long-range order sets in [41, 42]. $\chi$ of the system fails to follow the typical CW law above $T_N$ up to a certain critical temperature known as Griffiths temperature ($T_{\text{GP}}$). However, with increasing $H$, the downturn in the $\chi^{-1}$ vs $T$ data softens and becomes gradually indistinguishable from the high-$T$ PM regime [30, 43]. The application of a sufficiently high $H$ polarizes the spin on the outside part of the clusters, leading to the suppression of the signature of GP in the $\chi^{-1}$ vs $T$ data [30, 37]. The cluster-like FM component is masked at higher-$H$ by the linear increase of the PM contribution of the matrix [42].

It is known that the inverse susceptibility in the GP obeys a power law behaviour characterized by an exponent ($\lambda$) [17, 23],

$$\chi^{-1} \propto (T - T_{\text{GP}})^{\lambda}$$

where, $0 < \lambda < 1$ for $T_N < T < T_{\text{GP}}$. In the PM phase, $\lambda \rightarrow 0$, and equation (1) turns into usual CW law. $T_{\text{GP}}$ can be

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**Figure 3.** Main panel presents the Arrot plot ($M^2$ vs $H/M$) of the sample recorded at different temperatures. Inset: variation of spontaneous magnetisation ($M_s$) with $T$ below $T_N$.

**Figure 4.** (a) Inverse susceptibility versus temperature data recorded under $H = 1$ kOe. The inset shows the same data measured under 100 Oe. (b) Shows inverse susceptibility data measured in different values of the applied field. Inset shows the log–log plot of inverse susceptibility as a function of $(T/T_{\text{GP}}^0 - 1)$. 

obtained from the PM phase by setting $\lambda \sim 0$, which is close to the PM Curie temperature. We have plotted $\log(\chi - 1)$ against $\log(T/T_0 - 1)$ (inset of figure 4(b)) and the value of $\lambda$ is obtained from the slope of the linear fit using equation (1) (solid red line fit). In PM and GP regions, the obtained values of $\lambda$ are 0.006 and 0.91 respectively (using $T_0 = 147$ K). Similar $\lambda$ value is earlier reported for Heusler alloys Fe$_{2-x}$Mn$_x$CrAl showing Griffiths-like behaviour [44]. A large difference between $T_N$ and $T_{GP}$ is observed in NiFeTiSn along with a value of $\lambda$ close to unity in the GP regime. This signifies the strong deviation from the CW behaviour and point towards the robustness of the GP in this material. The deviation of $\chi^{-1}(T)$ from CW law prevails even for $H$ as high as 10 kOe. This feature is also unusual compared to other systems where such deviation vanishes for $H \gtrsim 1$ kOe [22, 23].

Galitski et al [45] studied the GP in the dilute magnetic semiconductor in the light of magnetic polarons. The magnetisation in the GP is found to be weak and it follows a relation:

$$M(H, T) \propto \exp \left[ -\frac{B T}{H} \right]$$

(2)

where, $B$ is a constant. It is to be noted that equation (2) does not take into account the pinning effect between the magnetic clusters which is relevant in the low field regime. Hence, the $M(T)$ data measured at lower fields ($H = 50$, 100 and 200 Oe) cannot be fitted well using equation (2) [46]. In figures 5(a) and (b) we have plotted $M$ versus $T/H$ along with linear fit for $H = 500$ Oe and 1 kOe within the temperature range 160–220 K. The value of the constant $B$ obtained from fitting is 28.4(3) and 54.5(4) Oe K$^{-1}$ for $H = 500$ Oe and 1 kOe respectively, which are similar to the earlier reported values for other GP systems [46, 47].

To confirm GP in NiFeTiSn, 100 K $M(H)$ isotherm has been plotted in figure 5(c). $M$ is found to obey the predicted GP behaviour given by,

$$M(H) = M_0 + aH^\eta$$

(3)

where $M_0$ is the non-zero spontaneous magnetisation and $\eta$ is an exponent [48, 49]. The best fit between 20 to 70 kOe yields the exponent $\eta$ to be 0.78. This value of $\eta$ is close to the value of $\lambda$ obtained from equation (1), and such closeness of these two exponents is common in GP [50]. Most importantly, a power law variation of $M(H)$ curve (equation (3)) is a clear deviation from the linear $M(H)$ behaviour expected in a pure PM region (CW law) [48, 51].

To get further idea of the nature of the magnetic state in NiFeTiSn, we performed field-cooled-field-stop memory (FCFCS memory) measurement as shown in figure 6 [52, 53]. Initially, the sample was cooled under $H = 100$ Oe from 300 to 2 K with intermediate stops at $T_{\text{stop}} = 6, 50$ and 100 K for $t_\text{w} = 3600$ s each. The magnetic field was turned off at $T_{\text{stop}}$ which results in a step-like magnetization curve ($M_{\text{FC}}^{\text{stop}}$). After reaching 2 K, the sample was further heated in presence of $H = 100$ Oe without any stops ($M_{\text{FC}}^{\text{mem}}$) (see figure 6). Interestingly, the heating curve, $M_{\text{FC}}^{\text{mem}}$, does not show any anomaly at the stopping temperatures where the sample was allowed to stop during cooling. This points to the fact that no FC memory is present in the system, ruling out the possibility of a spin-glass or superparamagnetic state.

Figure 5. (a) and (b) Shows $\log M$ versus $T/H$ plot of NiFeTiSn under the applied field of $H = 500$ Oe and 1 kOe. The solid line is the best linear fit using the relation (2). (c) Shows magnetisation as a function of field at $T = 100$ K following a power-law behaviour.
Figure 6. FCFS memory curves at three stopping temperatures, $T_{\text{stop}} = 6, 50$ and $100$ K. The inset shows an enlarged view of the low temperature data.

We further studied the thermoremanent magnetisation (TRM), $M_{\text{TRM}}$, to characterize the GP [40, 54]. The protocol involves cooling the sample from well above the magnetic transition temperature in the presence of cooling field, $H_{\text{cool}}$. The field is removed below $T_N$, and the magnetisation is measured while heating under $H = 0$. In the present case, this protocol was repeated for three different cooling fields, $H_{\text{cool}} = 100, 200$ and $500$ Oe (figure 7(a)). The zero-field measurements have the advantage that the contributions from the PM susceptibility are suppressed compared to an in-field measurement. All the three curves (recorded in zero field while heating after being cooled in different values of $H_{\text{cool}}$) show sizeable TRM below $300$ K. At temperature above about $210$ K, these curves are practically indistinguishable. Below about $200$ K, the curves start to diverge from each other and a hump-like feature is observed. On field cooling, the FM clusters of the GP are created favourably with the direction of $H_{\text{cool}}$. When the sample is heated from the lowest temperature after setting $H = 0$, the clusters remains pinned and provide us a remanent magnetisation. The TRM eventually disappears above a certain temperature when the GP is destroyed. The presence of TRM supports the existence of magnetic clusters in the material.

The short-range FM regions in the GP drastically influence the dynamics of the magnetic susceptibility. In the GP, the time required to reverse the effective spin of clusters would be larger, resulting in a non-exponential decay of the spin-auto correlation function [55]. For randomly diluted ferromagnets, this decay has been calculated to be of the form $\sim \exp(-B^{0.5})$ and $\sim \exp[-A \ln \rho^{1.5}]$ for 3D Heisenberg and Ising spin systems respectively [56]. Figure 7(b) highlights the isothermal remanent magnetisation (IRM) data for NiFeTiSn within the GP regime (50, 150, 225, and 250 K). We cooled the sample from $300$ K in presence of $H = 50$ Oe to a particular temperature of measurement, subsequently the time variation of $M$ was recorded for $3600$ s after switching off the magnetic field. Good linear fit is obtained for $\log M$ versus $t^{0.5}$ data for all the temperatures. The upper inset of figure 7(b) presents the plot for $\log M$ versus $t^{0.5}$, and its non-linear nature rules out the Ising nature of the spins within the clusters. We can conclude that the interaction between spins in the GP regime are Heisenberg-like. The TRM and IRM measurements provide strong evidence in favour of the presence of FM clusters within the PM matrix [40, 55].

Figure 8 shows the zero-field heat capacity ($C_p$) data measured between $2–300$ K, where $C_p$ decreases monotonically with decreasing $T$. $C_p$ tends to saturate above $250$ K and its value at $300$ K is found to be $105$ J mol$^{-1}$ K$^{-1}$. This value is marginally higher than the classical Dulong–Petit value of $12R = 99.8$ J mol$^{-1}$ K$^{-1}$ ($R$ is the universal gas constant). Such deviation in $C_p(T)$ is a signature of phonon anharmonicity in presence of disorder [57, 58]. Notably, $C_p$ does not show any $\lambda$-like anomaly at around $T_N$. However, $C_p/T$ vs $T^2$ data show a shallow minimum below $T_N$ (see inset), which possibly related to the AFM-like order in the system. The $C_p/T$ vs $T^2$ varies linearly between $T = 12$ and $20$ K, and the Sommerfeld coefficient $\gamma$ obtained from this linear region is found to be $26$ mJ mol$^{-1}$ K$^{-2}$ [59]. This value is twice as high than the full Heusler Fe$_2$TiSn [5]. The absence of $\lambda$-like anomaly in the heat-capacity data is not uncommon among Heusler family of compounds [60, 61].
In many instances, spin glass are found to show a broad hump like feature in the heat capacity ($C_p$ versus $T$). In our data, we rather observe a sharp rise in the $C_p/T$ vs $T^2$ plot, which is not a standard feature of the glassy magnetic phase [61]. Such low-$T$ upturn below $T_N$ can be taken as an evidence for the onset of bulk magnetic ordering in the sample. Due to the presence of Griffiths-like short range correlation, a significant amount of magnetic entropy is already released when the sample is cooled down to $T_N$ from 300 K. Such pre-existing magnetic correlation will effectively weaken the signature in $C_p$ at $T_N$ [62, 63].

### 3.3. Electrical resistivity and thermopower

The $\rho(T)$ behaviour of NiFeTiSn (see figure 9(a)) is found to have a negative ($d\rho/dT < 0$) temperature coefficient of resistivity (TCR). $\rho(T)$ is also characterized by a sharp rise below 12 K. Several quaternary and half Heusler compounds, such as CoFeCrGa [14], CoFeMnSi, CrVTiAl [64],YPD3Sb, LuNiSb [65], show negative TCR over a wide $T$-range. Interestingly, the nature of the $\rho(T)$ data above 20 K in NiFeTiSn is found to be rather unusual as compared to the common semiconductors. In a semiconductor, the carriers are thermally excited across an energy gap, and one generally finds an exponential (or sometimes stretched exponential) type of $\rho(T)$ data where the $\rho$ versus $T$ plot is convex upward. This has been exemplified by an exponential resistivity behaviour (red dashed line) in figure 9(e). On the contrary, NiFeTiSn shows a concave upward nature, where the curvature is opposite to that of common semiconductors.

The negative TCR in disordered metallic systems is often considered in the framework of generalized Faber–Ziman theory for liquid metals and further extended for amorphous and crystalline solids by Cote and Meisel [65–70]. In this model, the resistivity of highly resistive metals can be expressed as

$$ \rho(T) = \exp(-2W(T)) (\rho_0 + \Delta_{ep}) \quad (4) $$

where,

$$ W(T) = \frac{3h^2}{8\pi^2mk_Bn_D} \rho_0^2 \left[ \frac{1}{c^2 - 1} + \frac{1}{2} \right] z \, dz + \Delta_{ep} $$ \quad (5)

Here, $\rho_0$ is the residual resistivity due to the scattering of electrons with static defects, and $\Delta_{ep}$ is the inelastic electron–phonon interaction term. $2W(T)$ is the Debye–Waller exponent averaged over all the scattering vectors $k$ of the conduction electrons. In equation (5), $m$ stands for the ionic mass, while $h$, $k_B$, and $n_D$ are respectively Planck constant, Boltzmann constant and Debye temperature. For disordered metals with high value of $\rho_0$, $\Delta_{ep}$ is negligible as compared to $\rho_0$. Since $2W(T)$ increases with increasing $T$, equation (4) will lead to a negative TCR. We have fitted equation (4) to the $\rho(T)$ data with an approximation that $\Delta_{ep}$ is negligible as compared to $\rho_0$ for NiFeTiSn. The fitting (figure 9(a)) converges well between 70 to 300 K and we obtain $\rho_0 = 270 \mu\Omega \text{cm}$, $<k^2> = 5.88 \times 10^{13}$ m$^2$ and $\theta_D = 327$ K.

To explain the low-$T$ upturn in $\rho(T)$, we have plotted the data (5–50 K) as a function of $\ln T$ (figure 9(c)). A linear variation indicates the upturn to be logarithmic in nature. Such upturn may arise due to weak localization or Kondo effect [71].
Notably, NiFeTiSn presents a small (~ −3%) negative MR at $T = 10$ K as shown in figure 9(f). With increasing $T$, the magnitude of the MR decreases and it is about −2% at 200 K. However, the MR turns negligible at 300 K. The finite negative MR at 200 K, which is well above the magnetic ordering temperature, is in line with the short range magnetic correlations.

$T$ dependence of Seebeck coefficient ($S$) was measured for NiFeTiSn and shown figure 9(b). The negative value of $S$ indicates that electron is the dominant carrier. $S$ increases with $T$ following a quasilinear behaviour up to room temperature. The maximum value of $|S|$ is found to be around 25 $\mu$V K$^{-1}$ at room temperature. The absolute value of $S$ at 300 K for NiFeTiSn is comparable to that of potential thermoelectric Heusler alloys such as Fe$_2$VGa and Ru$_2$NbGa ($\sim 25$ $\mu$V K$^{-1}$) [72]. NiFeTiSn has appreciable value of thermoelectric power factor $PF = \frac{S^2}{\rho}$ of 2.5 $\mu$W cm$^{-1}$ K$^{-2}$ at 300 K. This value of $PF$ is comparable to good thermoelectric materials such as semimetallic Ru$_2$NbGa and Ru$_2$NbAl [60, 73, 74]. We have also measured the transverse Hall resistivity ($\rho_{xy}$) and its variation with $H$ is shown in figure 9(d). We have calculated the values of carrier concentration ($n$) and Hall mobility ($\mu_H$) at $T = 10, 300$ K, and they are found to be $n = 2.3 \times 10^{21}$, $2.2 \times 10^{21}$ cm$^{-3}$ and $10.2, 11.5$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Negative Hall coefficient also supports the result obtained from $S(T)$ measurement, i.e., electrons are the dominant carriers in NiFeTiSn. The $\mu_H$ obtained for NiFeTiSn is comparable to other reported Heusler compounds [75, 76].

4. Discussion

There are only limited number of reports for Griffiths-like phase in Heusler alloys and compounds. They include systems such as Fe$_2$VGa, Fe$_2$VAl and Fe$_2$CrAl-based alloys. The present NiFeTiSn is a quaternary Heusler compound, and to our knowledge, FeMnCrAl is the only other compound showing GP in this series [44]. However, unlike NiFeTiSn, FeMnCrAl has a long range FM ground state. The cusp like feature around 7 K both in the ZFC and FC magnetisation data indicates that the ground state is AFM-like in NiFeTiSn (figure 2(a)).

So far, most of the experimentally reported intermetallic GP compounds order ferromagnetically at low temperature [23, 30, 44], and AFM GP compounds are relatively lesser in number. The signature of GP above $T_N$ is quite convincingly established from our study. The archetypal signature of GP is evident from the $\chi^{-1}$ versus $T$ data, where we observe a strong downturn from linear CW law below $T_GP$ (≈275 K). We also observe a power law variation of inverse susceptibility ($\chi^{-1} \sim T^{1-\lambda}$), which is a common protocol to establish a GP. The magnetisation of NiFeTiSn also obeys the scaling law, $ln M \sim \frac{1}{T}$ roughly in the temperature range between $T_N$ and $T_GP$.

Microscopically a GP is characterized by spatially isolated non-interacting FM clusters in a PM matrix. Therefore, it is pertinent to show that our compound is devoid of any long-range order between $T_N$ and $T_GP$. If we extrapolate the high $H/M$ Arrot plot data (above $T_N$) towards the origin (see figure 3), they strike the ordinate at negative values of $M^2$, indicating the lack of spontaneous magnetisation. Further proof opposing the long range ordered phase between $T_N$ and $T_GP$ is obtained from our Mössbauer spectra. The distinct singlet line obtained both at high-$T$ (300 K) and low-$T$ (80 K) confirms the lack of a long range magnetic order in these $T$ range for NiFeTiSn. The Mössbauer line recorded at 80 K ($\gg T_N$) is found to be significantly wider than that of 300 K data. This increase in the width possibly indicates the growth of the short range FM clusters with decrease in $T$. Similar observation were reported in the Heusler compounds Fe$_2$VGa and Fe$_2$VAl [77, 78] and Eu-doped Ca$_3$Co$_2$O$_6$ [79].

The unexpected magnetic anomaly observed close to room temperature could also be associated to the existence of FM impurity phase with a $T_C$ close to room temperature. However, such possibility can be convincingly ruled out in light of the following evidences: (A) lack of spontaneous magnetisation (for $T > T_N$) indicates the absence of long-range FM ordering and thus excludes the possibility of the existence of a FM impurity phase. (B) The Mössbauer spectra have singlet line at 300 K and 80 K. The line is sharp and symmetric. Had there been any FM impurity or ordering, one should see a splitting or broadening of the line. $^{57}$Fe Mössbauer spectra is quite sensitive to any ordered impurity phase. For example, even 1% Fe (non-enriched) doping in BaTiO$_3$ can produce significant splitting of the singlet line [80]. However, in case of NiFeTiSn, we find the Mössbauer line which can be well fitted by a single Lorentzian function (see figure 1(b)). This certainly signifies that the sample does not order magnetically at least down to 80 K within the accuracy of the Mössbauer technique. The lack of magnetic order is the most important characteristics of a Griffiths-like phase and the present data supports the presence of GP in the studied compound. (C) Careful observation and analysis of x-ray powder diffraction data for NiFeTiSn reveals the absence of any major impurity phase (within the accuracy limit of the experimental technique). All the peaks observed can be indexed to the cubic LiMgPdSn type Heusler structure [81]. (D) The nonexponential decay of $M$ with time above $T_N$ indicates isolated non-frustrated spin clusters [55] and it rules out long-range ordering of the FM impurity phase. Above all, $\chi$ and $M$ follow the appropriate scaling laws of a GP as opposed to the behaviours of an FM state.

Magnetic relaxations measured in the GP-regime of the sample (see figure 7(a)) does not obey a simple exponential law. Instead, we observe $M(t)$ to follow $\exp[-\frac{1}{\sqrt{T(t)}}]$ type of variation with time. Theoretical arguments indicate that such form of relaxation is a signature of Heisenberg type spin system within the FM clusters of the GP [18, 19]. As an example, REBaCo$_2$O$_7$ (RE = rare-earth) compounds show similar relaxation behaviour, and the Heisenberg nature of the spin system is further verified by means of neutron scattering experiments [82].

NiFeTiSn has a simple cubic structure at room temperature and it does not show any change in its lattice symmetry as a function of temperature [16]. The full Heusler compound Fe$_2$TiSn is an important example where ferromagnetism originates from antisite disorder. Our PXRD analysis indicates...
about 17% antisite disorder between Ti and Fe sites. Such disorder can create isolated Fe-rich magnetic clusters leading to Griffiths-like phase. Interestingly, NiFeTiSn shows GP from 280 K, which is very close to the Curie temperature of Fe$_2$TiSn. DFT based calculations indicate small value of moment at the Ni site of the quaternary compounds NiFeTiZ ($Z = P, As, Si, Ge$) [83]. As compared to Fe$_2$TiSn, one Fe atom is replaced by Ni in NiFeTiSn, and this dilution of Fe atoms might be responsible for the lack of long range FM order developing around 260–280 K. Instead, isolated FM clusters are formed in the latter compound leading to Griffiths-like phase. It is worth noting that GP in Fe$_2$VGa and some of its dopants is also related to antisite disorder between Fe and V sites [84].

In the original conjecture laid down by Griffiths, the short range FM clusters in the GP can eventually lead to a long-range ordered FM ground state on lowering the temperature. However, the situation can be different if the ground state attains antiferromagnetism. There are numerous examples in the literature on such AFM Griffiths-like phase, and the present NiFeTiSn is found to be a new addition to the list. The most pertinent question regarding the AFM GP is the nature of the magnetic ground state. In the literature, there are reports where the short range FM clusters continue to coexist with the long-magnetic groundstate. In the AFM Griffiths-like phase, it is instrumental for spin canting when the sample attains a long-range order below $T_N$. It is to be noted that the value of spontaneous magnetisation obtained from the Arrot plot is quite small, which corresponds to the weak ferromagnetism below $T_N$ due to spin canting [86, 87]. However, we also have to rule out the possibility of the sample being a simple ferrimagnet. In case of a ferrimagnet, there have to be two antiparallel sublattices with different magnetic moment values. Consequently, the net moment will be non-zero. For the present NiFeTiSn, there can be Ni and Fe sublattices. The band structure calculations of similar compounds such as NiFeTiZ ($Z = P, Si, Ge, As$) shows that the moment at the Fe site ($m_{Fe}$) is much larger than that of the Ni site ($m_{Ni}$) [83]. Therefore the net moment ($m = m_{Fe} - m_{Ni}$) will be significant. Since our data indicates very small value of $M_S$, the scenario for a ferrimagnetic state is improbable.

NiFeTiSn shows a negative thermal variation of $\rho$, but does not resemble a general activated behaviour found in semiconductors. Rather $\rho(T)$ shows an unusual nature where the curve is concave downwards. Fe$_2$TiSn, on the other hand, shows metallic behaviour below about $T_C$, and shows negative temperature coefficient behaviour of resistivity ($d\rho(T)/dT < 0$) in the PM region [88]. The metallicity in Fe$_2$TiSn is believed to be connected to the long range FM order. Since NiFeTiSn does not order ferromagnetically at high temperature, it retains its negative temperature coefficient of resistivity down to low temperatures. The $\rho(T)$ data between $T_{CG}$ and $T_N$ can be fitted with Cote–Meisel model [67] for disordered systems. The scattering of conduction electrons with static site disorders and/or isolated magnetic clusters is possibly responsible for the rather unusual $\rho(T)$ variation in this temperature window. Interestingly, the Seebeck coefficient of NiFeTiSn is found to be negative as compared to the positive value in Fe$_2$TiSn,
although the magnitudes of thermopower are comparable [76]. As shown in figure 9(b), the magnitude of $S$ increases with increasing temperature following a quasi-linear behaviour up to room temperature. For heavily doped semiconductors (parabolic band, energy-independent scattering approximation) with degenerate character of electrons/holes, the magnitude of $S$ generally increases monotonically with increasing $T$ [76, 89, 90].

In conclusion, we report an extensive investigation on the cubic Heusler compound NiFeTiSn by means of magnetic, Mössbauer, electrical and thermal transport properties measurements. The work establishes a Griffiths-like phase that exists over a wide range of temperature (15–275 K). The ground state of the compound is found to be canted AFM type in nature, and our work indicates that the FM clusters due to GP disappear with the advent of this canted AFM state below $T_N$.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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