Study of the magnetocaloric effect in intermetallics *RTX* (*R* = Nd, Gd; *T* = Sc, Ti ; *X* = Si, Ge)

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ABSTRACT

A detailed study of the magnetocaloric properties of six compounds of the intermetallic family *RTX* (*R* = Nd, Gd; *T* = Sc, Ti ; *X* = Si, Ge) has been undertaken: NdScSi, NdScGe, GdScSi, GdScGe, $GdSc(Si_{0.5}Ge_{0.5})$ and $Gd(Sc_{0.5}Ti_{0.5})Ge$. The magnetic entropy changes at the Curie temperature T_C and the refrigerant capacities signal that they are competitive magnetocaloric materials, showing that an improvement can be obtained by tuning the composition, as $Gd(Sc_{0.5}Ti_{0.5})Ge$ presents the best properties. These magnetocaloric variables fulfill the scaling equations with the critical parameters corresponding to the universality classes to which the ferromagnetic transitions belong (3D-XY, 3D-Heisenberg, Mean field). For each compound, a universal curve has been found for the rescaled magnetic entropy changes obtained at different applied fields, whose behavior at temperatures below T_C indicate the relevance of taking into account the demagnetization field. Finally, it has been demonstrated that the rescaled magnetic entropy changes for the compounds which share the same universality class collapse onto a single universal curve.

Keywords:

Rare-earth scandium silicides; Rare-earth scandium germanides; Magnetic properties; Magnetocaloric effect; Magnetorefrigerant materials

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1. Introduction

There is currently a wide interest in the development of new magnetocaloric materials which can be the core of new magnetic refrigerators meant to replace the ones based on the classic gas expansion-compression cycles. These new refrigerators can compete in compactness, effectiveness and energy consumption, being at the same time more environmentally friendly. This search has turned from looking into materials with first order magnetic phase transitions (where the change in the magnetic entropy as a consequence of the application of a magnetic field can be huge) to studying compounds presenting second order ones (where the change is of a lesser degree). The main reason behind this is that the thermal hysteresis in the first cases is a drawback when designing a practical prototype [1, 2].

In this quest, intermetallic materials, among many others, are being designed looking for second order ferromagnetic transitions with Curie temperatures as close as possible to room temperature (see [1, 3] for revisions on materials). When studying the possibility that a particular compound might be of application to this end, it is not only important to obtain the value of the maximum entropy change $\left|\Delta S_M^{pk}\right|$ for a particular applied field but the refrigerant capacity as well, *RC*. Moreover, if the knowledge of the field dependence of ΔS_M and *RC* contributes, on the one hand, to the extrapolation of the experimental results obtained with certain fields to higher/smaller ones, on the other, gives an insight of the physics of the transition as it is related to the critical behavior of the phase transition through the critical parameters which define the proper universality class to which it belongs. In particular, they scale following the equations [2, 4, 5]

$$\Delta S_M^{pk} \propto H^{1+(1/\delta)(1-1/\beta)} \tag{1}$$

$$RC \propto H^{1+1/\delta} \tag{2}$$

where β and δ are the critical parameters associated to the spontaneous magnetization and the critical isotherm, respectively.

$$M_S(T) \sim |t|^{\beta} \qquad (T < T_C), \tag{3}$$

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

with $t = (T - T_C)/T$ being the reduced temperature

Thorough research (both theoretical and experimental) has shown that many materials with a ferromagnetic second order phase transition present a universal curve

ΔS_M as a function of temperature when measured at different applied magnetic fields [2, 4, 6, 7]. This is why a field of concern among the scientific community is the correct evaluation of the magnetic field-induced isothermal entropy change, ΔS_M [4]. Indirect methods based on the acquisition of isothermal $M(H)_T$ or isofields $M(T)_H$ magnetization measurements are widely used as they are easily accesible and the entropy change can be obtained from the Maxwell relation:

$$\Delta S_M(\mathrm{T}, \Delta \mathrm{H}) = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH \qquad (5)$$

In particular, it is quite common in literature not to take into account demagnetization factors, which have been demonstrated to lead to non-precise results in ΔS_M [8] or to non-universal curves [9] when the demagnetization factors are non negligible. Other factors, such as the presence of other minority phases, also affect the experimental results and, therefore, their interpretation [10, 11].

This work has two main aims: the first one has to do with the evaluation of the magnetocaloric variables ΔS_M and RC for a series of intermetallics of the family RTX (R = Nd, Gd; T = Sc, Ti ; X = Si, Ge), taking well into account possible misleading effects (demagnetization, other phases), and establishing their potential as magnetocaloric materials; the second one is to extend the study to the evolution of the magnetocaloric variables with the applied magnetic field in order to obtain a complete information and, finally, check whether they follow the scaling relations with the critical parameters which have already been established for these compounds [12, 13].

2. Samples and experimental techniques

The materials studied in this work are all polycrystalline alloys. Six compositions have been prepared: NdScSi, NdScGe, GdScSi, GdScGe, $GdSc(Si_{0.5}Ge_{0.5})$ and $Gd(Sc_{0.5}Ti_{0.5})Ge$. The details about the growth, quality and samples preparation can be found in [12, 13]. It is important to stand out that they are single phase save for the two samples containing Gd and Si, where a 2-3 Vol.% of $Gd_{5-x}Sc_xSi_3$ was present as a secondary phase.

Magnetization (M) measurements have been carried out in a VSM (Vibrating Sample Magnetometer) by Cryogenic Limited under external applied magnetic fields H_a ranging from 0 to 2 T, in order to better compare the results with literature. The temperature region covered has been 30-300 K for Nd-based compounds and 100-400 K for the samples

containing Gd. In order to have a good coverage of the critical region, isotherms have been collected for $\Delta T = 1$ K over a range of about ± 30 K around T_C while $\Delta T = 10$ K has been used for the rest. The applied magnetic field H_a has been corrected for demagnetization effects and the internal field calculated using the relation $H_i = H_a - NM$, where M is the measured magnetization and N the demagnetization factor, which has been obtained from zero-field ac susceptibility measurements following the method described in [14, 15], extracting the maximum value of this magnitude (often referred as the Hopkinson/principal maximum) and using the relation $N = 1/\chi_{max}$. The so obtained H_i has been the one used for the magnetocaloric analysis, as it has been shown that the calculated entropy change without the correction is lower than the one obtained having accounted for the demagnetization field (specially at low fields) [8]. The magnetic susceptibility was measured with AC Measurement System Option in PPMS (Physical Properties Measurement System) by Quantum Design. The demagnetization factors found are shown in Table 1.

3. Experimental results and discussion

In previous studies on the critical behavior of these compounds performed with the same samples, it was already well established that each of the six compounds present a second order ferromagnetic transition [12, 13], in agreement with literature [16-21]. Figure 1 and 2 shows the magnetic entropy change as a function of temperature for the Nd- and Gd- samples, respectively. The positions of the Curie temperatures are well in agreement with previous studies (171K for NdScSi, 189 K for NdScGe, 325 K for GdScSi, 342 K for GdScGe, 343 K for $GdSc(Si_{0.5}Ge_{0.5})$ and 327 K for $Gd(Sc_{0.5}Ti_{0.5})Ge$) performed by this group and other groups. Table 1 contains the value of the maximum $\left|\Delta S_M^{pk}\right|$ for the highest field used $H_a \approx 2$T, together with the refrigerant capacity, calculated in two ways, as it is found in different papers in literature: RC_{Area} is the area enclosed by the ΔS_M vs. temperature curves in the temperature range enclosed by the full width at half maximum of the peak, while RC_{FWHM} is the product of $\left|\Delta S_M^{pk}\right|$ times the width of ΔS_M at half maximum. These results indicate that the Gd-based family has good magnetocaloric properties, comparable to other compounds based on Gd [22-25] and to the results obtained for two of the same compositions (GdScSi, GdScGe) found in [21], though the values presented here for RC_{Area} are slightly higher. It is worth noting that $GdSc(Si_{0.5}Ge_{0.5})$ and $Gd(Sc_{0.5}Ti_{0.5})Ge$ (especially the latter) give a significantly higher

refrigerant capacity showing that tuning the composition in this family improves their magnetocaloric properties. On the other hand, Nd-based compounds have a lower value. In order to make a general comparison with data published in literature for other compounds, we need to be able to extrapolate these values to higher fields. As explained in the introduction, it is extremely interesting to study the field dependence of these magnetocaloric properties following equations (1) and (2) because this will allow extrapolations. The critical exponents $\alpha, \beta, \gamma, \delta$ for these magnetic transitions were already found in previous works, and they are gathered in Table 2. We have checked that, in all cases, $\left|\Delta S_M^{pk}\right|$ and RC scale with those parameters, which is shown in Figs. 3 and 4 for some selected compounds. This behavior confirms the attribution of the different universality classes (short-range 3D-Heisenberg for the Gd-based compounds, short-range 3D-XY for NdScSi, and close to the long-range mean field for NdScGe). This allows us to extend our comparison in the following way: Franco *et al* [3] have presented a very detailed review of the magnetocaloric properties of many compounds for applied fields of 5 T. Our extrapolations for $\left|\Delta S_M^{pk}\right|$ for this field are presented in Table 1, allowing us to compare them with the values determined in other rare earth containing compounds (see Fig. 25 in [3]). The Gd family gives values similar to the ones presented there in the same temperature range (above room temperature) while the Nd family has values in the average of those presented in that review for the range 170-190K. This implies that they could be competitive magnetocaloric materials within their respective Curie temperature ranges.

The next step in this magnetocaloric analysis is to build up the master curves for the different compounds calculating, for each of them, the normalized curve for the magnetic entropy change by dividing it by the corresponding maximum for the different values of the maximum applied field and rescaling the temperature axis. It has been demonstrated that, in an ideal case, it should be enough to use one reference point, rescaling the temperature axis above and below the Curie temperature as [2]

$$\theta_1 = \frac{T - T_C}{T_r - T_C}, \qquad (6)$$

(the reference temperature T_r being selected as that corresponding to a certain fraction of ΔS_M^{pk}; in this case 0.5 has been used). Nevertheless, it has also been shown that in some experimental cases, where the material departs from the ideal behavior given by the

magnetic equation of state, the use of two reference temperatures T_{r1}, T_{r2} becomes necessary to construct the universal curves [4]

$$\theta_2 = -(T-T_C)/(T_{r1}-T_C) \quad T \leq T_C \qquad (7)$$

$$\theta_2 = (T-T_C)/(T_{r2}-T_C) \quad T > T_C$$

This last situation arises when, for instance, there is a non-negligible demagnetizing field or there is no single magnetic phase. Fig. 5 shows the normalized curves for NdScSi using one and two reference temperatures; likewise Fig. 6 for $GdSc(Si_{0.5}Ge_{0.5})$ (the results are similar for the other compounds). We can see that there is a good collapse around the Curie temperature with only one reference T_r but that there are some deviations in the low temperature part, which are subdued when using two references T_{r1}, T_{r2}. If increasing the applied field gives as a consequence an increase in the normalized magnetic entropy change (for a given value of the rescaled temperature), then the deviation is due to the presence of a demagnetization field [9, 21]; on the contrary, if the consequence is a decrease in the normalized entropy, then the physical origin of the deviation is the presence of other magnetic phases [10, 11]. In all cases, the entropy increases with the applied field, implying that the demagnetization field in these samples is important enough to be taken into account, confirming our strategy to calculate the refrigerant capacity from internal field data. The fact that even with two reference temperatures the collapse is not complete at low temperature values well below the peak is due to the fact that the magnetic equation of state is only valid in the near vicinity of the critical temperature [11]. Interestingly, even if in two samples [GdScSi, $GdSc(Si_{0.5}Ge_{0.5})$] there is a small amount of secondary phase, the results imply that only the main phase is responsible for the ferromagnetic transition, as no effect linked to the presence of other phases has been found.

In order to complete the magnetocaloric study, it has also been theoretically shown that the reference temperature T_r scales following relation[2]:

$$T_r \propto H^{1/(\beta+\gamma)} \qquad (8)$$

Fig. 7 shows, for some selected samples, how this scaling is fulfilled using the critical exponents collected in Table 2.

Finally, the normalized magnetic entropy curves for different materials which share the same universality class should collapse on one universal curve in the close vicinity of the critical temperature, as they share the critical exponents [5, 6]. Fig 8 shows the result with the four samples of the Gd-based compounds (which comply with the 3D-

Heisenberg class), confirming this theoretical universality. In the same figure, the Nd-based samples curves have also been superimposed, showing that NdScGe clearly deviates from this universality (which is logical as the difference in β and δ are important from the Heisenberg class to the nearly mean field one to which NdScGe belongs), while NdScSi nearly collapses on the rest, which is understandable as the critical exponents for 3D-Heisenberg and 3D-XY are very similar: β_{Heis}=0.365, β_{XY}=0.34, and δ_{Heis}=4.80, δ_{XY}=4.82.

Conclusions

We have shown that the intermetallic family *RTX* (*R* = Nd, Gd; *T* = Sc, Ti ; *X* = Si, Ge) presents interesting magnetocaloric properties, signalled by the magnetic entropy change at the Curie temperature as well as by the refrigerant capacity. It has been demonstrated that they fulfill the scaling equations with the critical parameters corresponding to the universality classes to which they respectively belong (3D-XY, 3D-Heisenberg, Mean field) and that universal curves can indeed be built up: on the one hand, for a given material as a function of the magnetic field and, on the other hand, for materials which share the same universality class.

Acknowledgments

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Table 1. Experimental values obtained for the peak entropy change $-\Delta S_M^{pk}$ and refrigerant capacities RC_{FWHM}, RC_{Area} obtained with an applied field of 1.9 T for the Nd-based compounds and 1.96 T for the Gd-based ones. N is the calculated demagnetization factor. In the last column, the extrapolated peak entropy change for an applied field of 5 T is presented, through the use of the scaling laws.

Compound	$-\Delta S_M^{pk}$ **(J kg^{-1} K^{-1}) [≈ 2 T]**	RC_{FWHM} **(J kg^{-1}) [≈ 2T]**	RC_{Area} **(J kg^{-1}) [≈ 2T]**	***N (g Oe/emu)***	$-\Delta S_M^{pk}$ **(J kg^{-1} K^{-1}) [5 T]***
NdScSi	1.96	47.35	36.48	78.60	3.84
NdScGe	1.20	35.13	26.32	48.22	2.42
GdScSi	1.90	133.20	100.08	2.82	3.70
GdScGe	2.04	135.35	100.36	19.14	4.00
GdSc($Si_{0.5}Ge_{0.5}$)	2.22	145.48	109.94	15.77	4.26
Gd($Sc_{0.5}Ti_{0.5}$)Ge	2.23	165.85	122.85	1.09	4.23

*Extrapolated values, using scaling laws

Table 2. Theoretical critical exponents [26-29] and experimental ones for the materials considered in this study [12, 13].

Universality class	α	β	γ	δ
Mean-field Model	0	0.5	1.0	3.0
3D-Ising	0.11	0.3265	1.237	4.79
3D-XY	-0.014	0.34	1.30	4.82
3D-Heisenberg	-0.134	0.365	1.386	4.80
NdScSi	-0.015	0.339	1.297	4.82
NdScGe	$\rightarrow 0$	0.446	1.146	3.57
GdScSi	-0.12	0.36	1.375	4.86
GdScGe	-0.134	0.372	1.305	4.80
$GdSc(Si_{0.5}Ge_{0.5})$	-0.135	0.372	1.307	4.81
$Gd(Sc_{0.5}Ti_{0.5})Ge$	-0.122	0.370	1.282	4.80

Figure captions

Fig. 1. Magnetic entropy change as a function of temperature for NdScSi and NdScGe, under different applied fields.

Fig. 2. Magnetic entropy change as a function of temperature for different applied fields, for GdScSi and GdScGe, $GdSc(Si_{0.5}Ge_{0.5})$ and $Gd(Sc_{0.5}Ti_{0.5})Ge$.

Fig. 3. Field dependences of the peak magnetic entropy change for some compounds. The values of β and δ for each compound are the ones presented in Table 2.

Fig. 4. Field dependences of the refrigerant capacity for some compounds. The values of δ for each compound are the ones presented in Table 2.

Fig. 5. Universal curve with the rescaled magnetic entropy changes for NdScSi using one (upper box) or two (lower one) reference temperatures.

Fig. 6. Universal curve with the rescaled magnetic entropy changes for $GdSc(Si_{0.5}Ge_{0.5})$ using one (upper box) or two (lower one) reference temperatures.

Fig. 7. Scaling law for the reference temperature T_r for some compounds. The values of β and γ for each compound are the ones presented in Table 2.

Fig. 8. Construction of the rescaled magnetic entropy changes for all compounds using a single reference temperature at $H \approx 2$ T.

Fig. 1

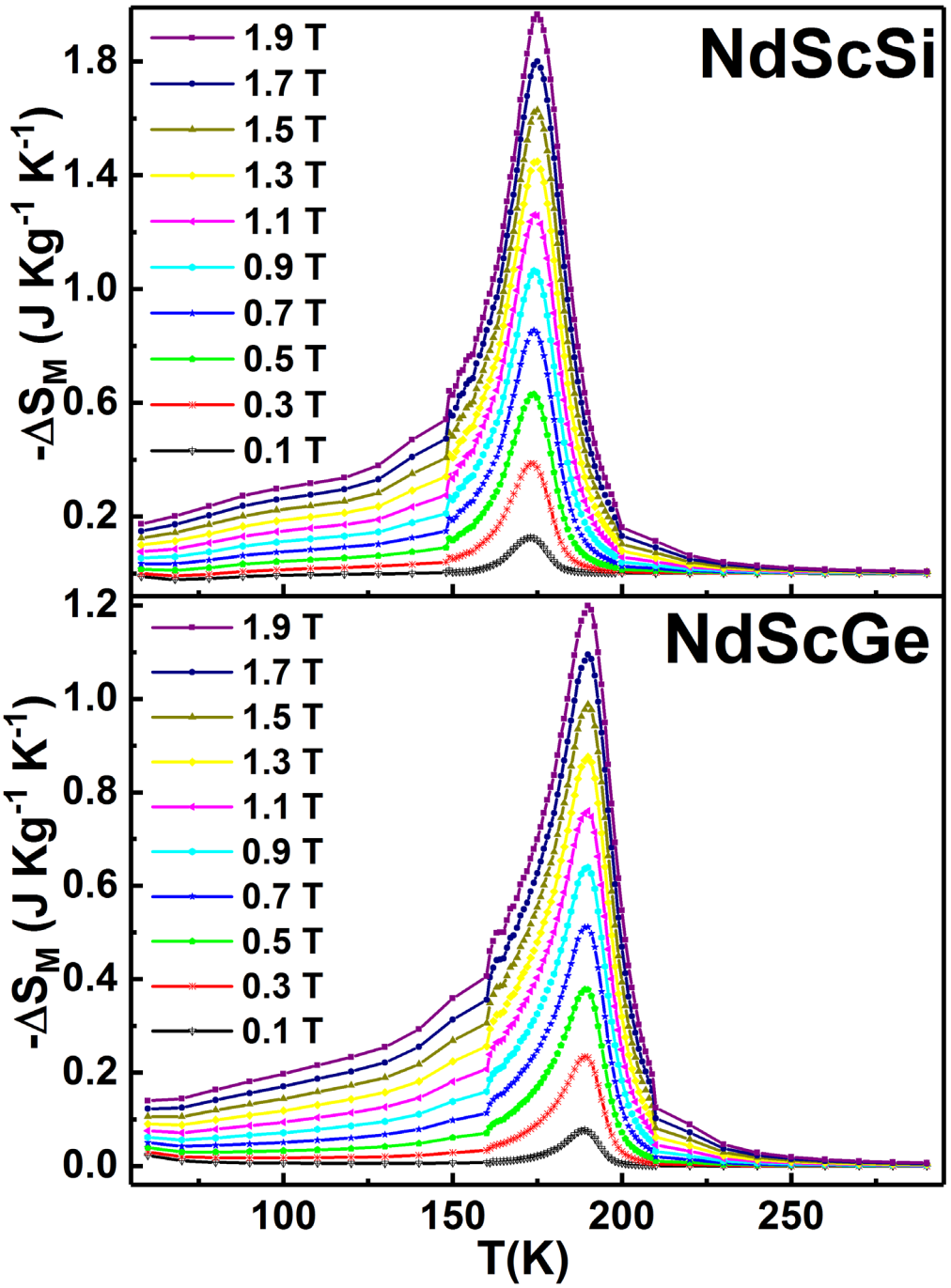

NdScSi
1.9 T
1.7 T
1.5 T
1.3 T
1.1 T
0.9 T
0.7 T
0.5 T
0.3 T
0.1 T
-ΔS_M (J Kg^-1 K^-1)
1.8
1.4
1.0
0.6
0.2
NdScGe
1.9 T
1.7 T
1.5 T
1.3 T
1.1 T
0.9 T
0.7 T
0.5 T
0.3 T
0.1 T
-ΔS_M (J Kg^-1 K^-1)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100
150
200
250
T(K)

Fig. 2

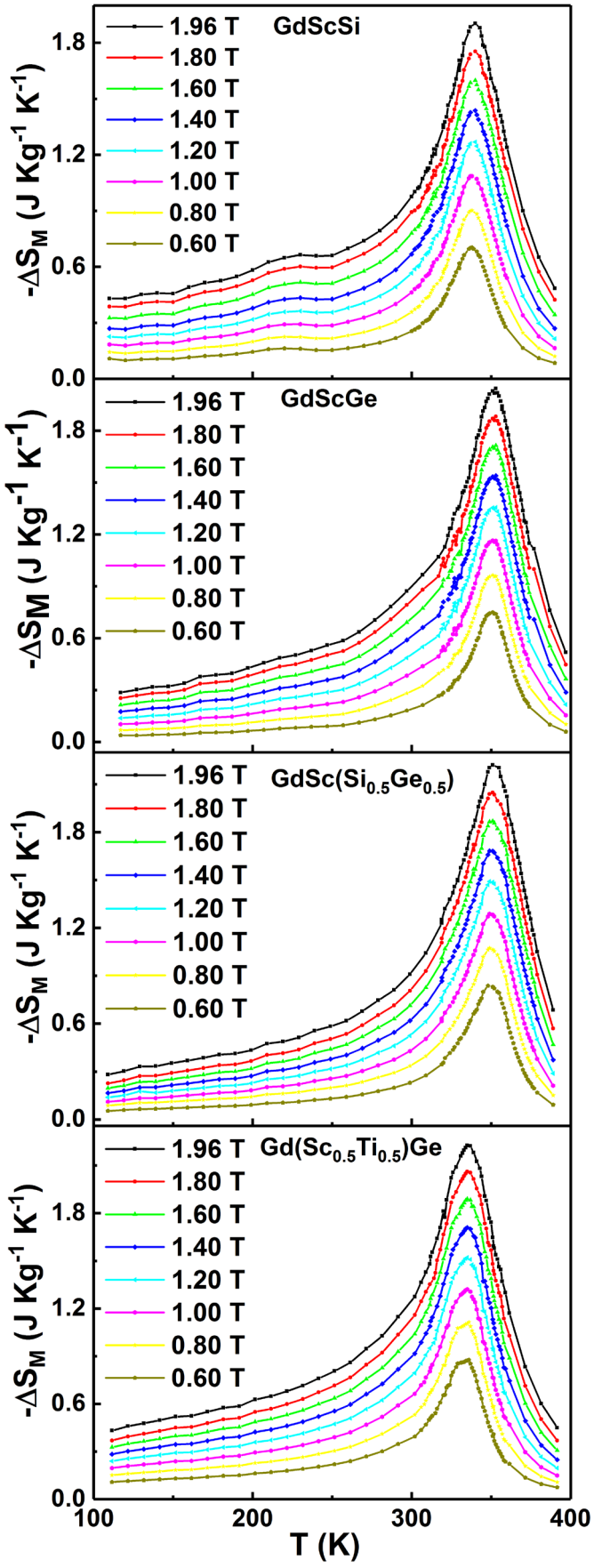
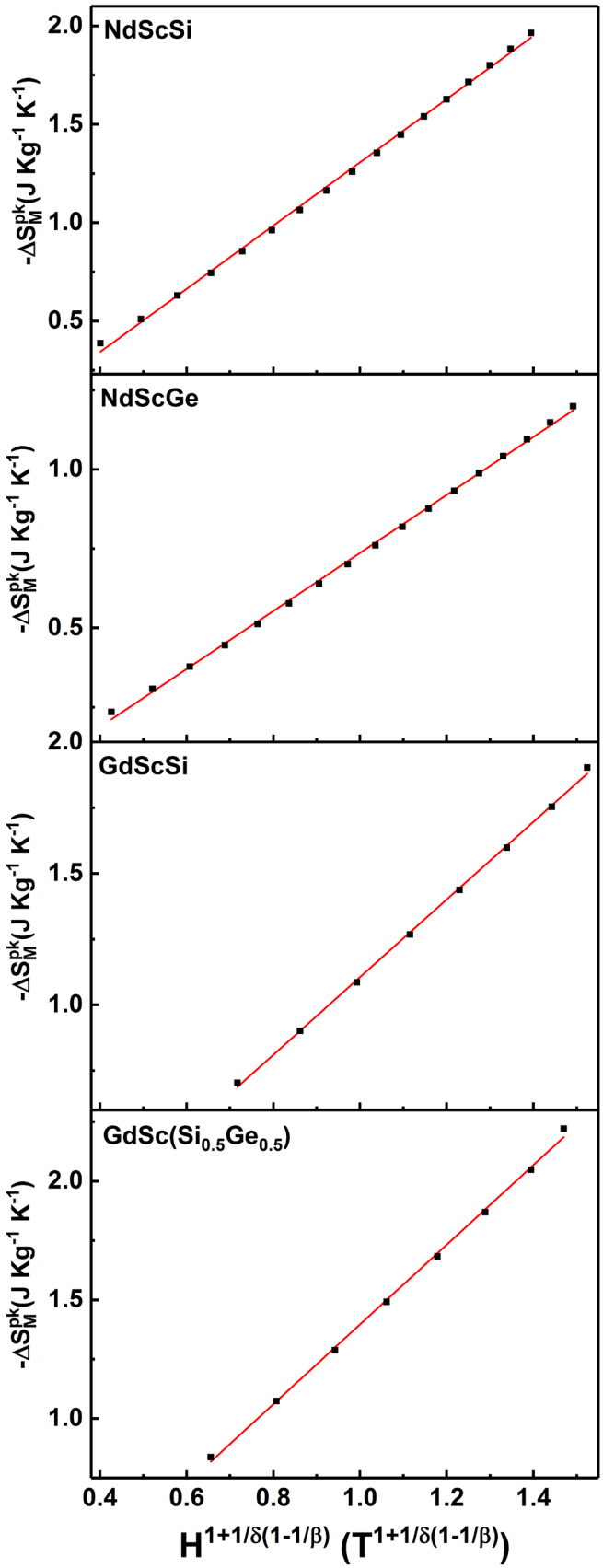

1.96 T
1.80 T
1.60 T
1.40 T
1.20 T
1.00 T
0.80 T
0.60 T
GdScSi
GdScGe
GdSc(Si0.5Ge0.5)
Gd(Sc0.5Ti0.5)Ge
-ΔSM (J Kg-1 K-1)
T (K)
0.0
0.6
1.2
1.8
100
200
300
400

Fig. 3


NdScSi
NdScGe
GdScSi
GdSc(Si0.5Ge0.5)
-ΔSMpk(J Kg-1 K-1)
H1+1/δ(1-1/β) (T1+1/δ(1-1/β))
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1.5
1.0
0.5
0.4
0.6
0.8
1.0
1.2
1.4

Fig. 4

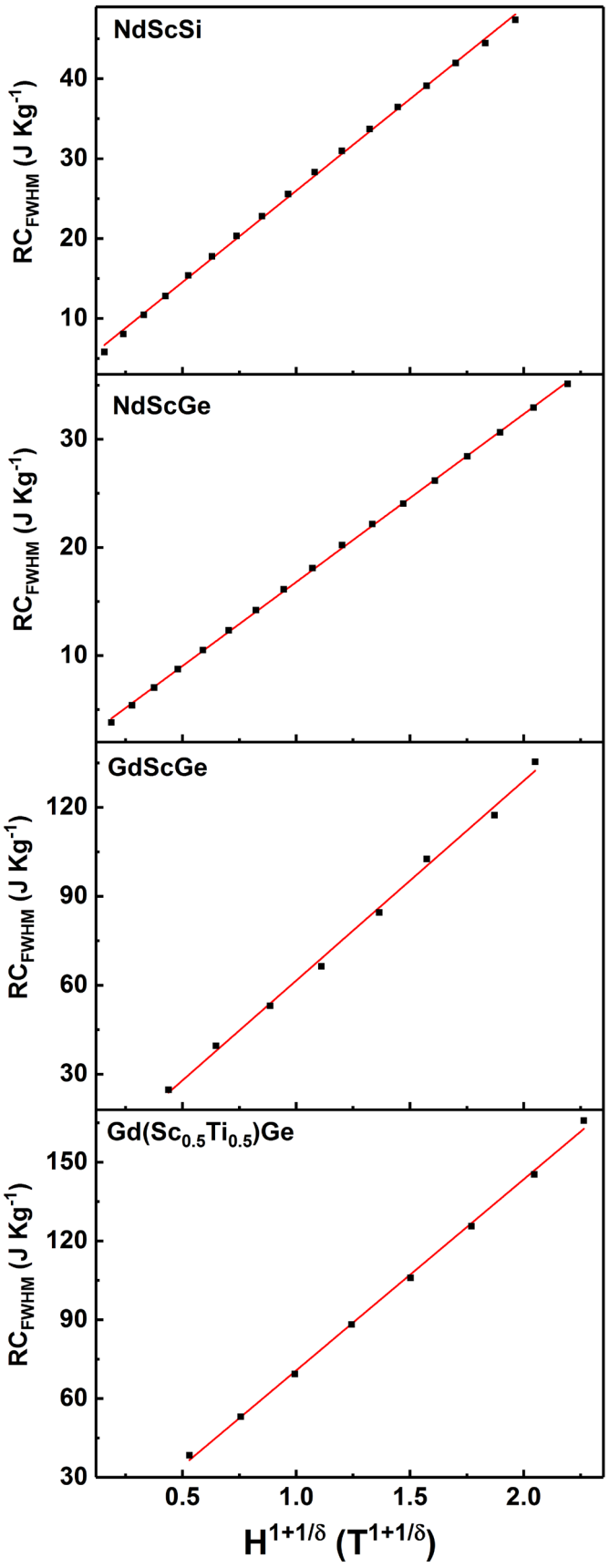


Fig. 5

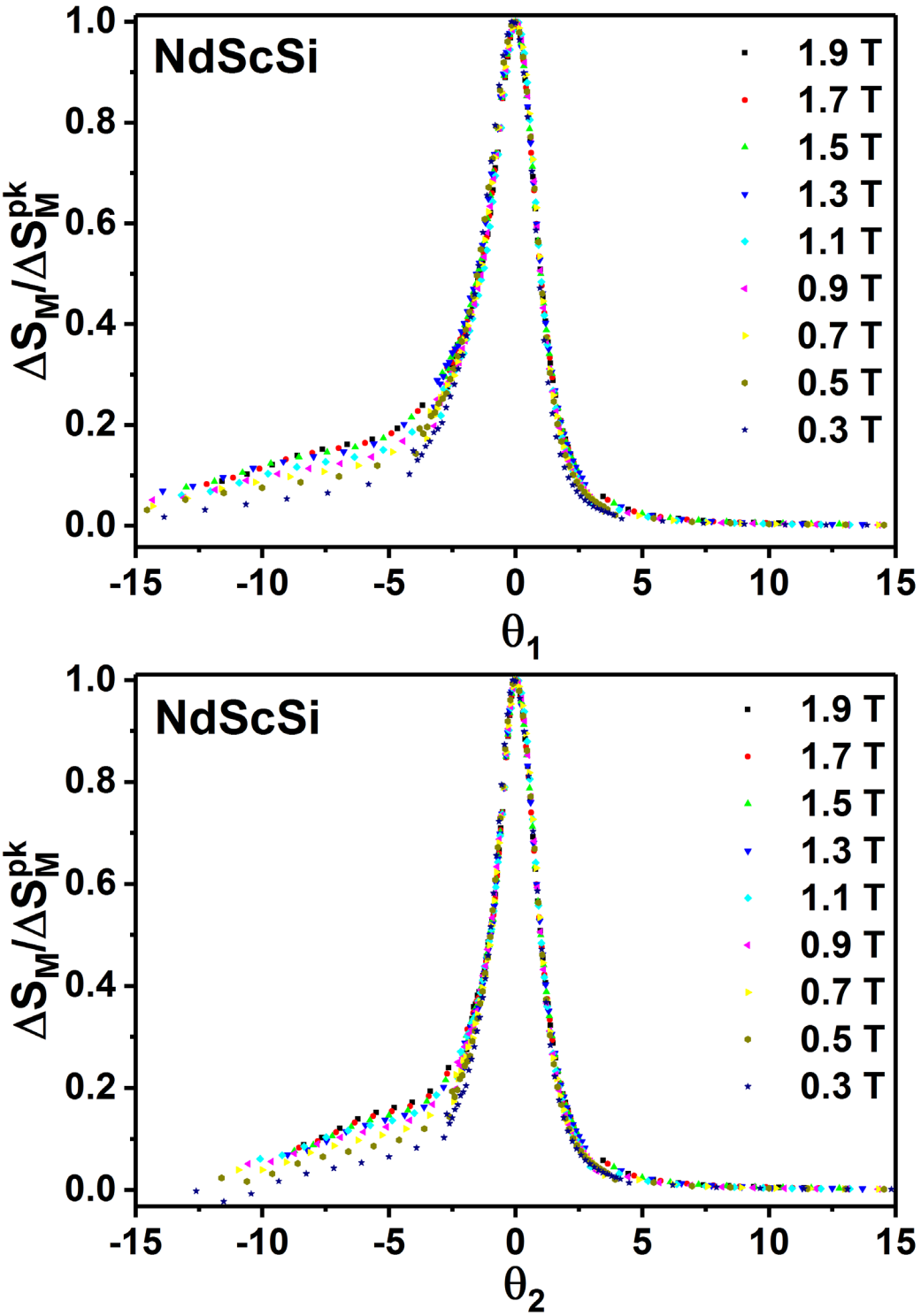

NdScSi
1.9 T
1.7 T
1.5 T
1.3 T
1.1 T
0.9 T
0.7 T
0.5 T
0.3 T
$\Delta S_M/\Delta S_M^{pk}$
θ_1
θ_2

Fig. 6

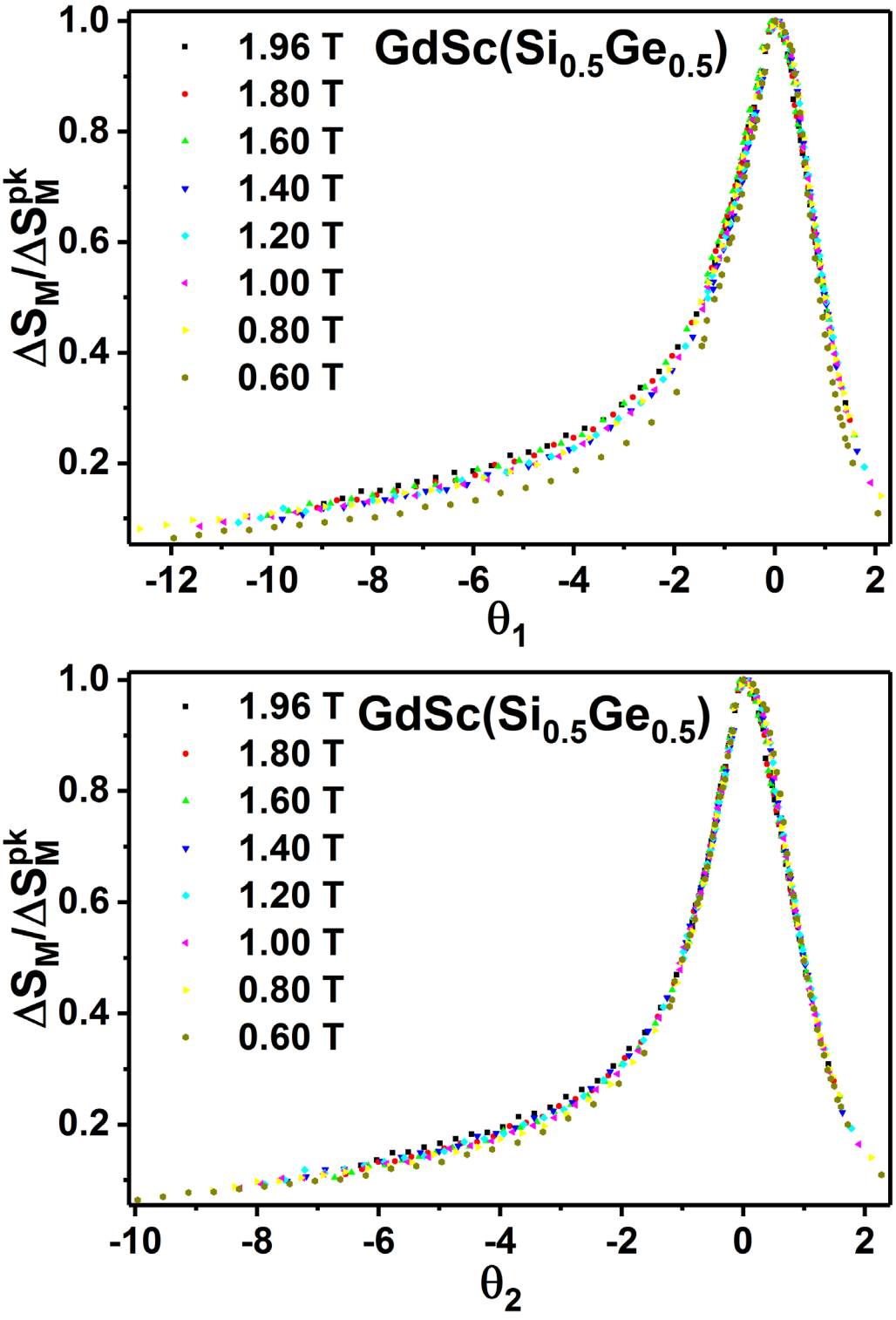

1.96 T
1.80 T
1.60 T
1.40 T
1.20 T
1.00 T
0.80 T
0.60 T
GdSc(Si0.5Ge0.5)
ΔSM/ΔSMpk
θ1
θ2

Fig. 7

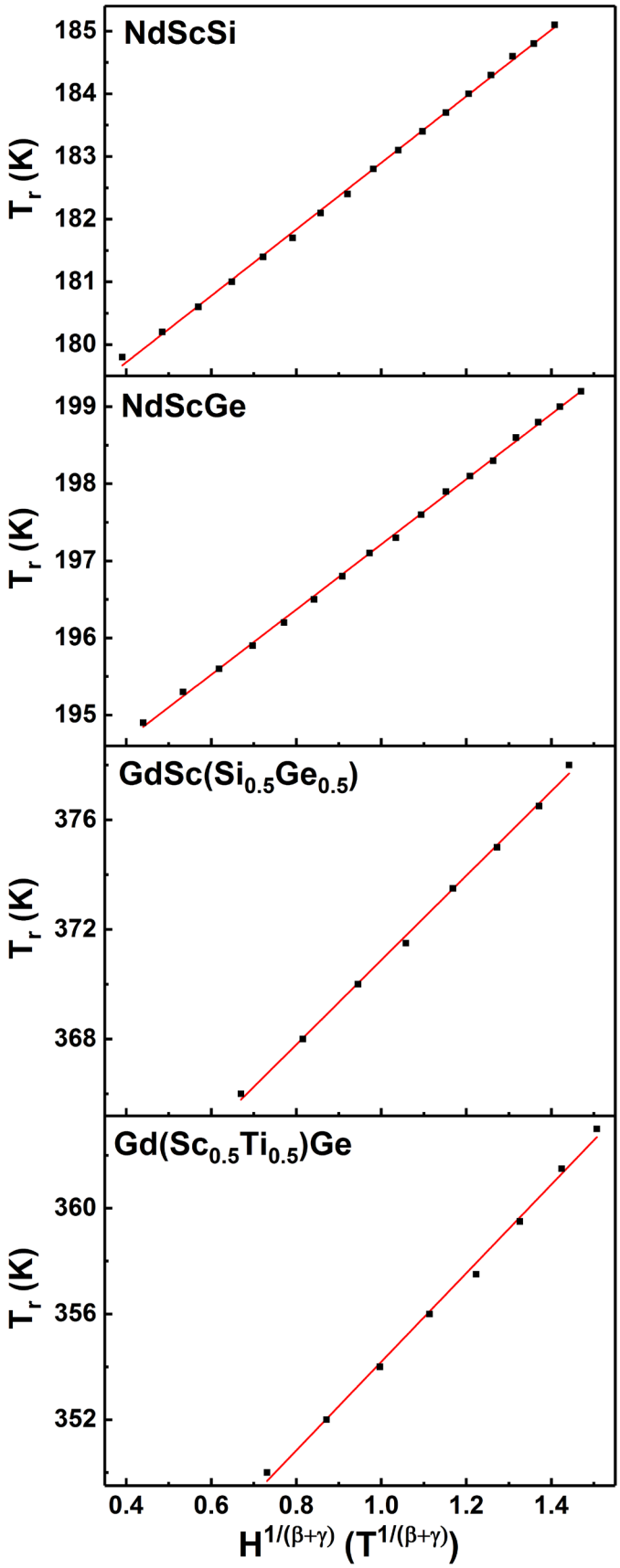
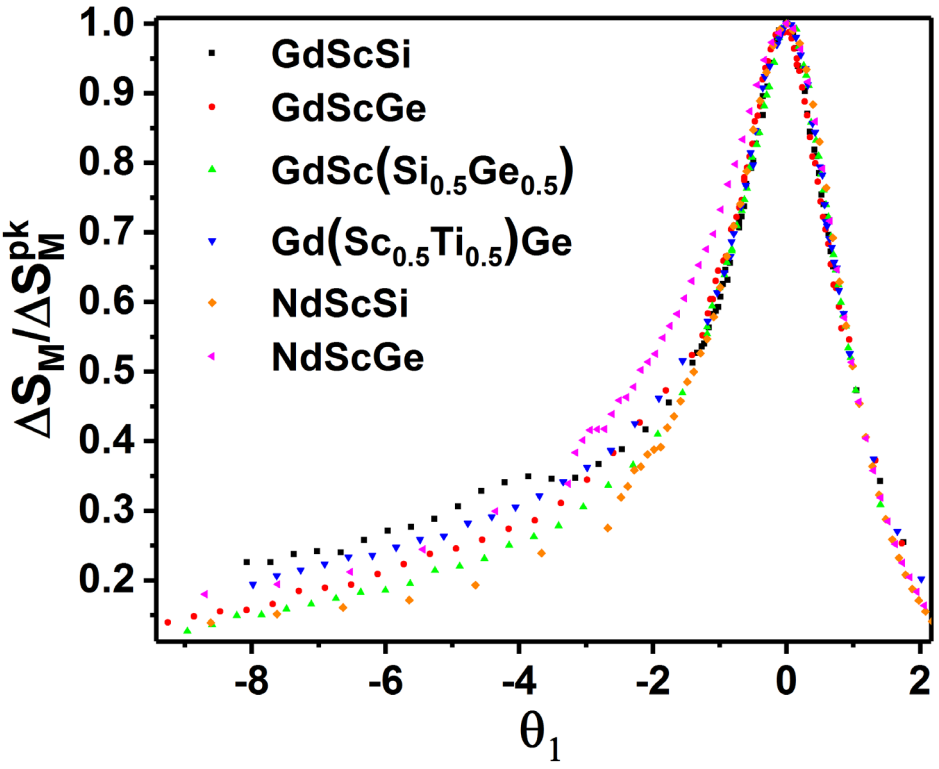


Fig. 8


GdScSi
GdScGe
GdSc(Si0.5Ge0.5)
Gd(Sc0.5Ti0.5)Ge
NdScSi
NdScGe
ΔSM/ΔSMpk
θ1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
-8
-6
-4
-2
0
2