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# Magnetocaloric effect in the ternary silicide $\text{Gd}_3\text{NiSi}_2$

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## A B S T R A C T

$\text{Gd}_3\text{NiSi}_2$  annealed sample has been investigated by magnetization, electrical resistivity and specific heat measurements. This study reveals its ferromagnetic behavior below  $T_C = 215$  K; only the gadolinium carries a magnetic moment with a saturation magnetization of  $7.19 \mu_B/\text{Gd mol}$ .  $\text{Gd}_3\text{NiSi}_2$  exhibits a magnetocaloric effect higher in magnetic entropy change than the one recently reported for  $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ . This ternary silicide can be obtained as metallic ribbons where the structural disordering modifies strongly its magnetocaloric properties.

## 1. Introduction

It is well known that some binary compounds existing in the Gd–Si and Gd–Ni systems present interesting magnetocaloric effect (MCE). These materials can be used in the magnetic refrigeration which is a promising alternative to conventional gas compression refrigeration [1–3]. For instance, the binary silicide  $\text{Gd}_5\text{Si}_4$  which orders ferromagnetically below  $T_C = 335$  K [4], a Curie temperature higher than that reported for gadolinium ( $T_C = 291$  K), shows an adiabatic temperature change  $\Delta T_{\text{ad}} = 3.1$  K in a magnetic field of 1.92 T [5]. These data suggest that  $\text{Gd}_5\text{Si}_4$  as Gd is an interesting candidate as magnetic refrigerant in the vicinity of room temperature. Moreover, the antiferromagnet  $\text{Gd}_3\text{Ni}$  ( $T_N = 99$  K) which has the highest Gd content among the compounds existing in the Gd–Ni system, is considered as a potential magnetic refrigerant material [6]. Considering these studies, it is interesting to investigate the magnetocaloric properties of the ternary compounds existing in the Gd–Ni–Si system and rich in gadolinium (50% or more in order to minimize the inactive thermal mass of solid).

At this day, two ternary silicides  $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$  and  $\text{Gd}_3\text{NiSi}_2$  correspond to the criterion defined above. The former, recently discovered by us, exhibits magnetocaloric properties [7]. It orders ferromagnetically at  $T_C = 310$  K and exhibits an interesting adiabatic temperature change of  $\Delta T = 3.1$  K in a magnetic field of 2 T. This value is comparable to that observed for  $\text{Gd}_5\text{Si}_4$ . The second,  $\text{Gd}_3\text{NiSi}_2$  was synthesized and characterized by X-ray diffraction by

Klepp and Parthé [8] but no investigation of its magnetic properties was performed. In this paper, we present and discuss the study of  $\text{Gd}_3\text{NiSi}_2$  by magnetization, electrical resistivity and specific heat measurements. Its magnetocaloric properties are compared to those reported for intermetallics being connected to the Gd–Ni–Si system. Moreover, in order to study the influence of the structural disorder on the magnetocaloric properties of  $\text{Gd}_3\text{NiSi}_2$ , we have prepared by melt-spinning technique metallic ribbons which have been characterized by magnetization measurements. The ferromagnetic materials presenting structural disorder are attractive for application as magnetic refrigerants [9,10]. For instance, the tailorable nature of their ordering magnetic temperature results from this disordering [11,12].

## 2. Experimental details

A polycrystalline  $\text{Gd}_3\text{NiSi}_2$  sample was synthesized by arc-melting a stoichiometric mixture of pure elements (purity above 99.9%) in a high-purity argon atmosphere. Then, the sample was turned and remelted several times to ensure homogeneity; the maximum weight loss due to the melting process was equal to 0.2%. Annealing was done for one month at 1073 K by enclosing the sample (*annealed sample*) in an evacuated quartz tube. A part of this sample was then remelted in a quartz tube under a high-purity argon atmosphere and quenched (melt-spinning technique) onto a rotating copper wheel with a surface speed of about 40 m/s. The obtained ribbons were roughly 20–30  $\mu\text{m}$  thick and 3 mm wide. The structural properties of annealed sample and ribbons were investigated by X-ray powder diffraction (Philips 1050-diffractometer and  $\text{Cu K}\alpha$  radiation).

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Magnetization measurements were performed on a powder, screened at 100  $\mu\text{m}$ , of the annealed sample and ribbon using a Superconducting Quantum Interference Device (SQUID) magnetometer in the temperature range 1.8–350 K and applied fields up to 4.6 T. The two powders were loaded in a paraffin resin in order to immobilize the randomly oriented particles during the magnetization measurements. Electrical resistivity was measured only on the annealed sample (a bar of  $1.5 \times 1.5 \times 5 \text{ mm}^3$ ) with a standard four probe method with silver paint contacts and a current of 10 mA in a temperature range 4.2–300 K. Heat capacity measurements were realized only on the annealed sample by a relaxation method with a Quantum Design PPMS system and using a two-tau model analysis. Data were taken in the 1.8–290 K temperature range. For these latter measurements, the sample was a plate of 10.8 mg weight obtained from the annealed sample. Finally, the very small thickness of the ribbons does not allow us to investigate with good accuracy their thermal properties.

### 3. Results and discussion

Fig. 1 displays the typical X-ray powder patterns of  $\text{Gd}_3\text{NiSi}_2$  samples obtained after annealing or melt-spinning process. The investigation of the annealed sample detects no parasitic phase and confirms that this ternary silicide crystallizes in the orthorhombic  $Pnma$  space group with the refined unit cell parameters  $a = 11.410 \text{ \AA}$ ,  $b = 4.158 \text{ \AA}$  and  $c = 11.322 \text{ \AA}$  which agree with those reported previously (see JCPDS no. 72-0218) [8]. The XRD pattern of the ribbons reveals only the presence of  $\text{Gd}_3\text{NiSi}_2$  (the investigation of the ribbons by microprobe analysis confirms their chemical homogeneity); this ternary silicide is stable after melting and rapid quenching. It is noted that the peaks of this last pattern are broadened and smaller than that observed for the annealed sample. This suggests the formation in the ribbon of a fine microstructure and a structural disordering; but the melt-spinning technique used here, does not allow to obtain an amorphous phase of  $\text{Gd}_3\text{NiSi}_2$ . Mean crystallites sizes ( $D_C$ ) forming the ribbon, were quantified by the Scherrer equation without a separation of strain:  $D_C = \lambda / (\beta \cos \theta)$ , where  $\lambda$  is wavelength of radiation ( $\text{Cu K}\alpha$ ),  $\beta$  the parameter of the broadening of the diffraction line, and  $\theta$  the diffraction angle. The errors were estimated to be  $\Delta D_C \cong 10\%$ . The crystallite sizes were about  $D_C = 9 \text{ nm}$  in the  $\text{Gd}_3\text{NiSi}_2$  ribbon whereas  $D_C = 20 \text{ nm}$  for the annealed sample.

Fig. 2 shows the temperature dependence of the magnetization  $M$  measured in an applied magnetic field  $\mu_0 H = 0.05 \text{ T}$  for the

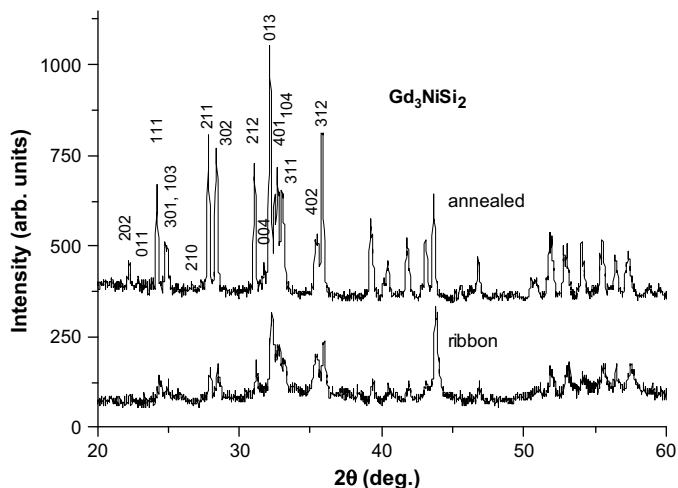


Fig. 1. X-ray powder patterns of  $\text{Gd}_3\text{NiSi}_2$  obtained after annealing (top) or after melt-spinning (bottom). For clarity, the Miller indexes are only given for  $2\theta < 35^\circ$ .

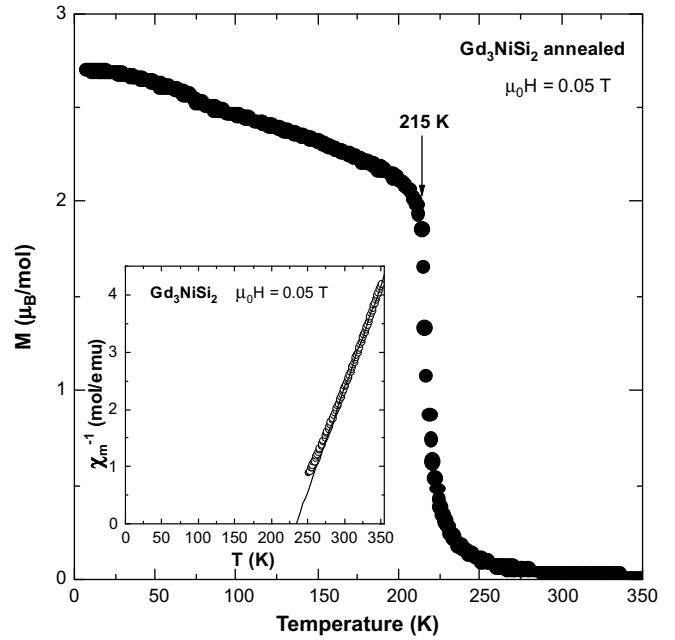
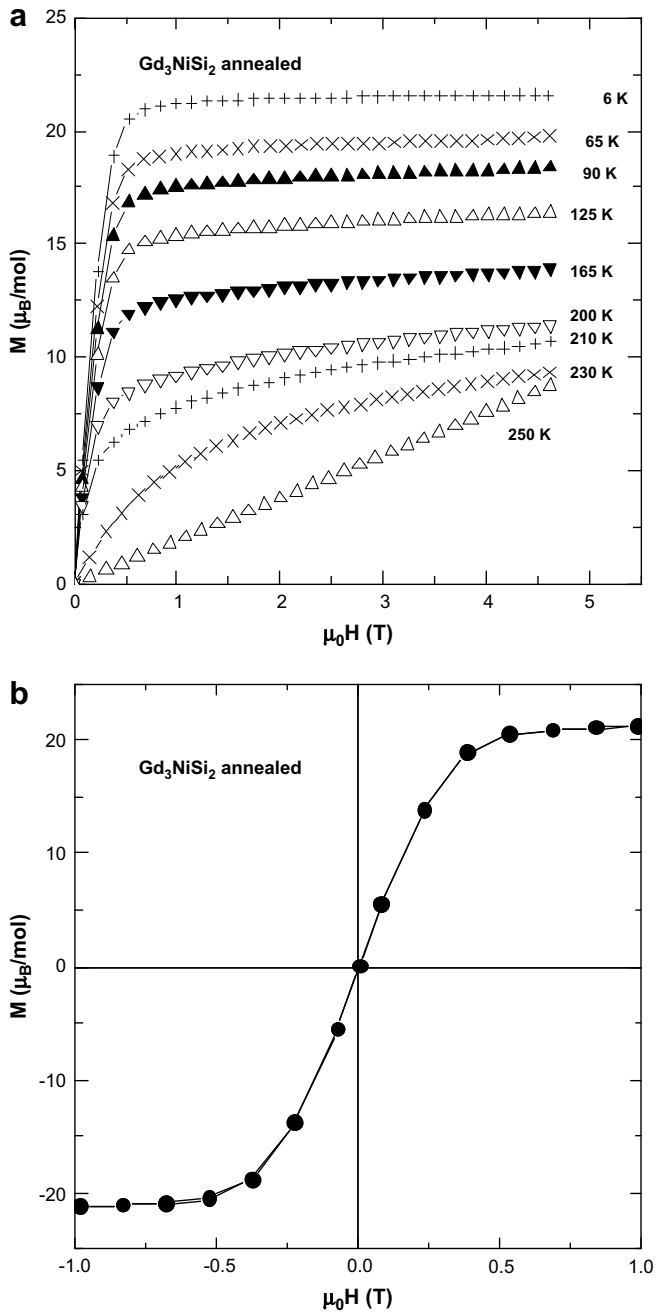


Fig. 2. Temperature dependence of the magnetization  $M$  measured in an applied magnetic field of  $\mu_0 H = 0.05 \text{ T}$  for  $\text{Gd}_3\text{NiSi}_2$  annealed sample. The inset presents the temperature dependence of the reciprocal magnetic susceptibility  $\chi_m^{-1}$ , measured with  $\mu_0 H = 1.5 \text{ T}$  (the solid line corresponds to the Curie-Weiss law as indicated in the text).

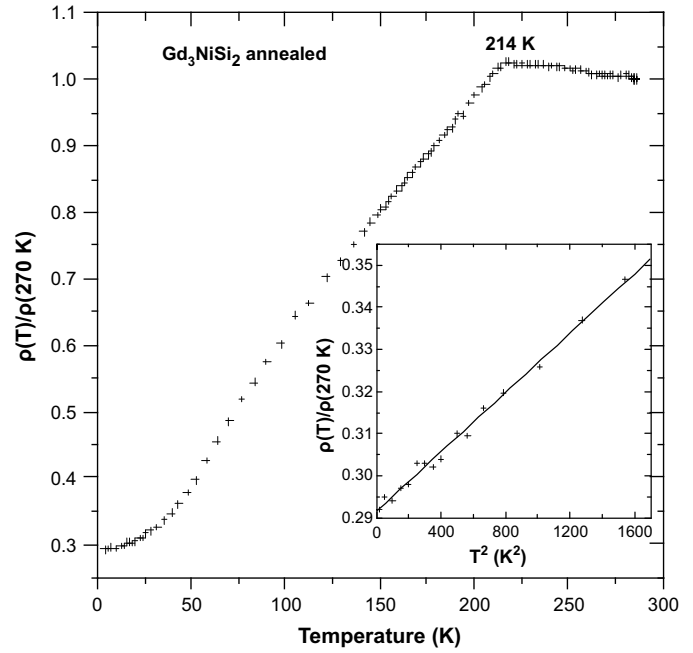
ternary silicide  $\text{Gd}_3\text{NiSi}_2$  (annealed sample). This curve  $M(T)$  presents a sharp increase of  $M$  at the Curie temperature  $T_C = 215 \text{ K}$  (temperature defined as the maximum in the derivative curve  $\partial(M)/\partial T$  versus  $T$ ). This  $T_C$ -temperature is smaller than that reported recently for the ternary compound  $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$  ( $T_C = 310 \text{ K}$ ) [7]. The curve  $M(T)$  exhibits also a small shoulder around 60–70 K attributed to the binary silicide  $\text{Gd}_5\text{Si}_3$  impurities, not detected by X-ray powder diffraction, which order magnetically in this temperature range [13]. The temperature dependence of the reciprocal magnetic susceptibility  $\chi_m^{-1}$  of  $\text{Gd}_3\text{NiSi}_2$  (inset of Fig. 2) follows above 275 K, a Curie-Weiss law (solid line) with  $\theta_p = 234 \text{ K}$  as a positive paramagnetic Curie temperature and  $\mu_{\text{eff}} = 7.98 \mu_B/\text{Gd mol}$  as magnetic effective moment. This last value is close to that calculated for a free  $\text{Gd}^{3+}$  ion ( $7.94 \mu_B$ ) and indicates that the magnetic contribution of Ni species is negligible. A similar remark was previously reported for the  $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$  ternary compound [7].

The ferromagnetic character of  $\text{Gd}_3\text{NiSi}_2$  annealed sample is confirmed by the field dependence of its magnetization  $M$  below  $T_C$  (Fig. 3(a)).  $M$  initially increases rapidly then tends to saturate at high fields. Below  $T_C$ , for instance at 6 K as shown in Fig. 3(b), this annealed sample behaves as a soft magnet with negligible coercivity and remanence. This behavior associated to the isotropic character of  $\text{Gd}^{3+}$ -ion is interesting for magnetic refrigeration. At 6 K, the measured saturation moment is  $21.58 \mu_B \text{ mol}^{-1}$  or  $7.19 \mu_B$  by Gd mol. This last value is slightly higher than that calculated  $g_J J = 7.00 \mu_B$  ( $g_J$  is the Landé factor and  $J$  the total angular momentum) for  $\text{Gd}^{3+}$  ion but is comparable to that reported for the binary compound  $\text{Gd}_3\text{Ni}$  ( $7.21 \mu_B$  by Gd mol) [6] or the ternary silicide  $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$  ( $7.10 \mu_B$  by Gd mol) [7]. A similar excess in the saturation moment was previously reported for the silicides ( $\text{Gd}_x\text{Tb}_{5-x}$ ) $\text{Si}_4$  [14], this excess was thought to be due to the contribution from the gadolinium 5d electrons resulting from the charge transfer between Gd sites and their neighboring ions. Finally, we note that  $M$  just above  $T_C$ , for instance at 230 K (Fig. 3(a)), does not vary linearly with the applied magnetic field. This observation indicates the existence of short-range magnetic correlations above  $T_C$ .



**Fig. 3.** Field dependence of the magnetization of  $\text{Gd}_3\text{NiSi}_2$  annealed sample at (a) various temperatures and (b) 6 K.

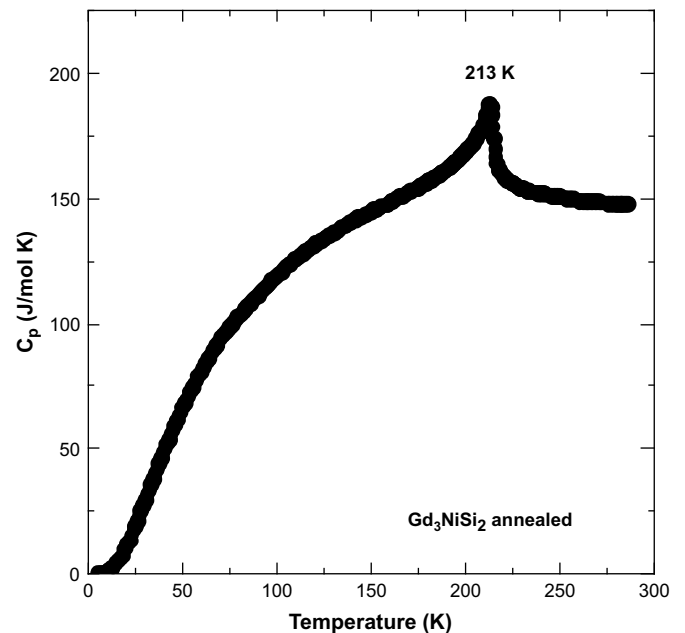
The existence of a ferromagnetic transition for  $\text{Gd}_3\text{NiSi}_2$  is confirmed by the temperature dependence of its reduced electrical resistivity presented in Fig. 4. A sudden change of slope is detected at 214 K (the temperature where the derivative curve  $\partial\rho/\partial T$  versus  $T$  exhibits a peak), in agreement with the  $T_C$  value extracted from the magnetization measurements. The decrease of  $\rho(T)$  below 214 K could be associated with the loss of spin disorder scattering of the conduction electrons owing to the appearance of a ferromagnetic transition. At low temperatures, below 35 K,  $\rho(T)$  data can be represented by a  $T^2$  function (inset of Fig. 4) in reasonable agreement with the quadratic temperature dependence expected for ferromagnetic material. Above 35 K,  $\rho(T)$  increases continuously but deviates from the linear dependence which characterizes the normal metals. A similar negative curvature of  $\rho(T)$  curve below  $T_C$



**Fig. 4.** Temperature dependence of the reduced electrical resistivity of  $\text{Gd}_3\text{NiSi}_2$  (annealed sample). The inset presents the  $T^2$  dependence of the resistivity at low temperature  $T < 35$  K (the solid line shows the linear dependence).

was observed recently for the other ternary silicide  $\text{Gd}_6\text{Co}_{1.67}\text{Si}_3$  [15]. This deviation detected in many compounds based on rare-earth elements [16] is attributed to the high value of their resistivity; the mean free path is short, of the order of a few interatomic distances.

The temperature dependence of the specific heat  $C_p$  of  $\text{Gd}_3\text{NiSi}_2$  (annealed sample) is shown in Fig. 5. The sharp  $\lambda$ -type maximum on the specific heat curve at 213 K agrees with the  $T_C$  Curie temperature of this ternary silicide determined above by magnetization and electrical resistivity measurements. The shape of the peak is typical for a second-order phase transition. At low



**Fig. 5.** The heat capacity  $C_p$  of  $\text{Gd}_3\text{NiSi}_2$  (annealed sample) between 1.8 and 290 K.

temperatures, below 18 K, the  $C_p/T$  versus  $T$  curve follows the Debye low-temperature approximation given by  $C_p/T = \gamma + \beta T^2$  where  $\gamma$  is the contribution from the conduction electron and  $\beta$  is the lattice contribution [17]. The fitting of  $C_p/T$  data yields to an electronic coefficient  $\gamma \cong 20 \text{ mJ/Gd mol K}^2$  which characterizes a metal.

The temperature dependence of the magnetization  $M$  of  $\text{Gd}_3\text{NiSi}_2$  ribbon was measured as for the annealed sample at  $\mu_0 H = 0.05 \text{ T}$  in zero-field-cooled (ZFC) and field-cooled (FC) modes; no irreversibility was detected by this measurement. The curve  $M(T)$  relative to the ribbon presents a different behavior (Fig. 6): a brutal but small increase occurs around 215 K (the  $T_C$  temperature of the annealed sample) then between 200 and 6 K,  $M(T)$  increases continuously with decreasing temperature. This measurement suggests that the ribbons contain two crystallographic forms of  $\text{Gd}_3\text{NiSi}_2$ ; one is crystallized involving an increase of  $M$  around 215 K and the other presents a great atomic disorder inducing a random distribution of the magnetic interactions leading to a progressive increase of  $M$  below 200 K. A similar behavior of  $M(T)$  was reported for Gd-based melt-spun ribbons [10] and for  $\text{GdAl}_2$  treated by high-energy-ball milling [18]. For low milling time, this  $\text{GdAl}_2$  sample contains an ordered ferromagnet phase and also an atomically disordered nanocrystalline material. Finally, we note that the magnetization at 6 K and at  $\mu_0 H = 0.05 \text{ T}$  ( $M = 7.64 \mu_B$  by  $\text{Gd}_3\text{NiSi}_2 \text{ mol}$ ) for the ribbon is higher than that determined in similar conditions for the annealed sample ( $M = 2.70 \mu_B$  by  $\text{Gd}_3\text{NiSi}_2 \text{ mol}$ ) (Figs. 2 and 6). At 6 K,  $M$  for the ribbons increases more rapidly at low applied magnetic field which explains this difference (inset of Fig. 6); certainly this difference is induced by the nanocrystalline character of the ribbon.

At 6 K, the field dependence of the magnetization  $M$  for ribbon reveals no magnetic hysteresis (see inset of Fig. 6).  $M$  for this sample does not saturate in a field of 4.6 T unlike to that observed for the annealed sample (Fig. 3). Moreover the measured moment  $18.40 \mu_B \text{ mol}^{-1}$  or  $6.13 \mu_B$  by Gd mol is smaller than that determined for the annealed sample ( $7.19 \mu_B$  by Gd mol). This difference could be associated to the presence of the atomically disordered nanocrystalline phase in the ribbon: (i) the excess of the magnetic moment by Gd-atom observed for the annealed sample and linked

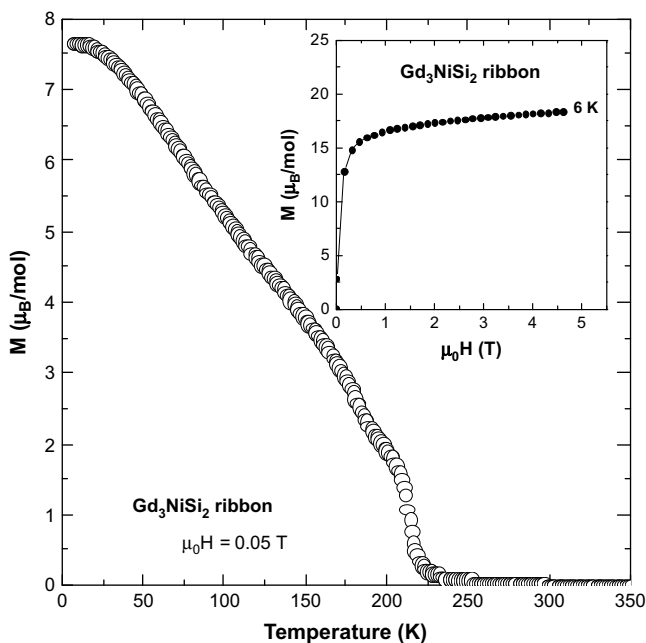


Fig. 6. Temperature dependence of the magnetization  $M$  measured in an applied magnetic field of  $\mu_0 H = 0.05 \text{ T}$  for  $\text{Gd}_3\text{NiSi}_2$  ribbon. The inset presents the field dependence at 6 K of the magnetization of this sample.

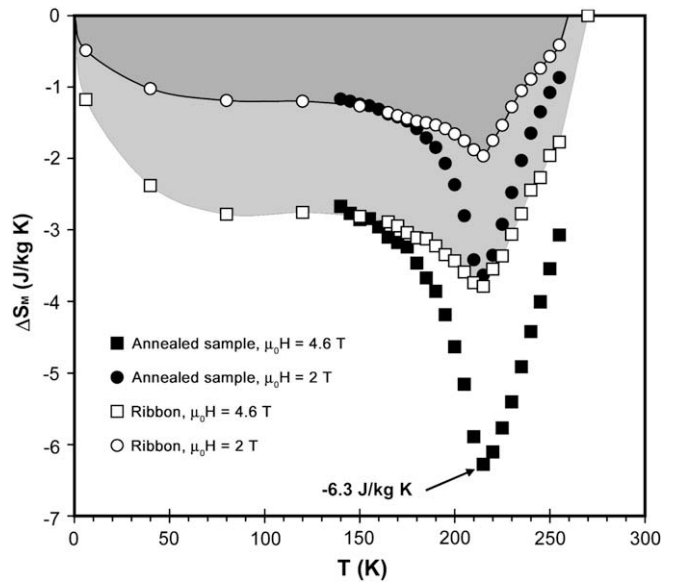


Fig. 7. Temperature dependence at  $\mu_0 H = 2$  and  $4.6 \text{ T}$  of the magnetic entropy change for  $\text{Gd}_3\text{NiSi}_2$  annealed sample and ribbon.

to the charge transfer between Gd sites and their neighboring ions disappears in this phase since it is disordered and (ii) moreover, this disorder will certainly change the number of nearest Gd-Gd neighbors and the relative distance between Gd atoms. This will probably cause a change of the direction of Gd moment from the originally parallel alignment (ferromagnet) to a randomly distributed configuration (antiferromagnetic interactions become possible); in these conditions a decrease of  $M$  is possible below  $T_C$ .

In order to determine the magnetocaloric properties of  $\text{Gd}_3\text{NiSi}_2$  annealed sample, its magnetization  $M$  was measured versus temperature between 140 and 260 K by step of 5 K and for applied field between 0 and 4.6 T by step of 0.15 T. The magnetic entropy change was calculated using the Maxwell formula,  $\Delta S_M = \int_0^{\mu_0 H} [\partial M / \partial T]_{\mu_0 H} d\mu_0 H$ , and the adiabatic temperature change,  $\Delta T_{ad}$ ,

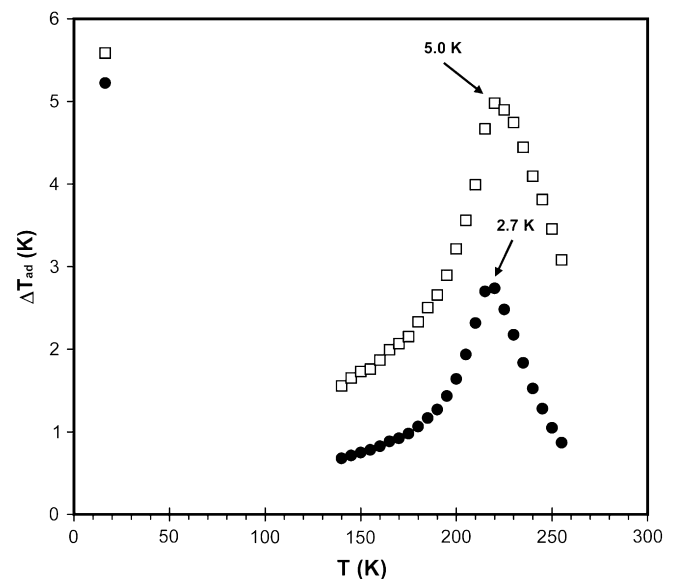


Fig. 8. Temperature dependence of the adiabatic temperature change for  $\text{Gd}_3\text{NiSi}_2$  annealed sample.



**Table 1**

Curie temperature, peak entropy change and adiabatic temperature change at  $\Delta H = 2$  T for  $Gd_3NiSi_2$  annealed and ribbon and others related materials.

	$T_C$ (K)	$\Delta S_M$ (J/kg K)	$\Delta T_{ad}$ (K)	$\Delta T_{ad}/T_C$	Ref.
$Gd_3NiSi_2$ annealed	215	-3.6	2.7	0.013	Present work
$Gd_3NiSi_2$ ribbon	215	-2.0	-	-	Present work
$Gd_6Ni_{5/3}Si_3$	310	-2.9	3.1	0.010	[7]
$Gd_6Co_{5/3}Si_3$	294	-2.8	3.0	0.010	[7]
$Gd_7Pd_3$	318	-2.5	-	-	[21]
Gd	294	-5.1	5.7	0.019	[22]

linked to the magnetocaloric effect was expressed as  $\Delta T_{ad}(T; 0 \rightarrow \mu_0 H) = -T/C_0(T)\Delta S_M(T; 0 \rightarrow \mu_0 H)$ , where  $C_0(T)$  is the heat capacity at zero field. As reported in Refs. [19,20], this indirect determination of the magnetocaloric properties is only an approximation; in some cases, the accuracy is in the range 20–30%.

Figs. 7 and 8 show the temperature dependence of  $\Delta S_M$  and  $\Delta T_{ad}$ , respectively, for  $Gd_3NiSi_2$  annealed sample. The curves of  $\Delta S_M(T)$  and  $\Delta T_{ad}(T)$  present one single peak at 215 and 220 K, respectively. The peak entropy change,  $\Delta S_M^{PEAK}$ , reaches  $-3.6$  and  $-6.3$   $J\,kg^{-1}\,K^{-1}$ , and the peak adiabatic temperature change,  $\Delta T_{ad}^{PEAK}$ , is 2.7 and 5.0 K for a field change of 2 and 4.6 T, respectively. Comparable values were observed for others ternary silicides and intermetallics based on gadolinium, as shown in Table 1.  $|\Delta S_M|$  of  $Gd_3NiSi_2$  annealed sample is higher than to those obtained for  $Gd_6Ni_{5/3}Si_3$  and  $Gd_6Co_{5/3}Si_3$  [7]. Also the value of the comparative ratio  $\Delta T_{ad}/T_C$  for this annealed sample is higher than those reported for the other ternary silicides but lower than that reported for pure gadolinium (Table 1).

The magnetic entropy change of  $Gd_3NiSi_2$  ribbon (Fig. 7) was also evaluated from a series of isothermal  $M(\mu_0 H)$  curves using the Maxwell formula. In addition to the peak at 215 K associated to the magnetic transition of the crystallized form of  $Gd_3NiSi_2$  as observed for the annealed sample, the curve  $\Delta S_M(T)$  relative to the ribbon exhibits a broad minimum between 50 and 150 K which can be attributed to the disordered form of  $Gd_3NiSi_2$ . The  $Gd_3NiSi_2$  ribbons exhibit lower peak value of  $\Delta S_M = -3.8$   $J\,kg^{-1}\,K^{-1}$  for  $\mu_0 H = 4.6$  T but a magnetocaloric effect that spans over a larger temperature range of approximately 200 K. Comparable behavior of  $\Delta S_M(T)$  curve was obtained recently for Gd-based melt-spun ribbons made of crystallized nanoparticles embedded into a disordered amorphous matrix [10]. As the full width at half minimum,  $\delta T_{FWHM}$ , of  $\Delta S_M(T)$  curve for the ribbon is greater than that of the annealed sample, thus giving rise to large relative cooling power (RCP) values of 890 and 390  $J\,kg^{-1}$  for  $\mu_0 H = 4.6$  and 2 T estimated from the product of  $|\Delta S_M^{PEAK}| \times \delta T_{FWHM}$ . These RCP values are, respectively, 570 and 200  $J\,kg^{-1}$  at the same magnetic fields for the annealed sample. This comparison shows the interest in magnetic refrigeration to obtain sample in ribbon form.

#### 4. Conclusion

The ternary silicide  $Gd_3NiSi_2$ , presents a ferromagnetic ordering at 215 K. This behavior is associated with a magnetocaloric effect higher than that observed for the other ternary compound  $Gd_6Ni_{5/3}Si_3$  existing in the Gd–Ni–Si system. Moreover, the synthesis of

$Gd_3NiSi_2$  as metallic ribbons leads to obtain a mixture containing two crystallographic forms of  $Gd_3NiSi_2$  (one is crystallized and the other presents a great atomic disorder inducing a random distribution of the magnetic interactions) and to extend the temperature range where this compound can be used as magnetic refrigerant.

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