

Structural and Magnetocaloric Properties of the New Ternary Silicides $Gd_6M_{5/3}Si_3$ with $M = Co$ and Ni

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Unlike $Gd_6Co_{5/3}Si_3$, which is obtained as a single phase after melting of the constituents, annealing under vacuum at 1073 K for 1 month is necessary to prepare the new ternary silicide $Gd_6Ni_{5/3}Si_3$. Indeed, after melting, this alloy is a mixture containing mainly Gd_3NiSi_2 and Gd_5Si_3 . These two compounds, $Gd_6M_{5/3}Si_3$ ($M = Co$ or Ni), crystallize with the hexagonal $Ce_6Ni_{2-x}Si_3$ -type structure. The crystal structure of $Gd_6Ni_{5/3}Si_3$, refined on a single crystal with space group $P6_3/m$ and unit cell parameters $a = 11.7433(1)$ Å and $c = 4.1857(1)$ Å, is characterized by infinite chains of face-shared trigonal prisms $[Gd_6]$ filled by silicon or nickel atoms. These chains run along the c -axis and extend as triangular columns by sharing rectangular faces in the ab -plane. Between these columns, infinite chains of face-shared octahedra of Gd atoms partially are filled by Ni atoms. The strong delocalization of the electron density of Ni observed in these latter chains has been attributed to high steric strains. No diffuse scattering nor superstructure were observed from electron diffraction experiments. The magnetization measurements reveal that (i) $Gd_6Ni_{5/3}Si_3$ orders ferromagnetically at 310 K, a Curie temperature higher than that observed for $Gd_6Co_{5/3}Si_3$ ($T_C = 294$ K) and pure gadolinium ($T_C = 294$ K); (ii) Ni as well as Co carries no magnetic moment; and (iii) these ternary silicides exhibit interesting magnetocaloric properties; for instance, the magnetic entropy (ΔS_m determined by magnetization measurements) of $Gd_6Ni_{5/3}Si_3$ is at a maximum around 312 K with values of $\Delta S_m = -2.93$ and -5.72 J/K kg at applied magnetic fields of 2 and 4.8 T, respectively. These properties are compared to those existing for the most famous magnetocaloric materials as Gd or $Gd_5Ge_2Si_2$.

Introduction

More than 30 years ago, Bodak et al. reported on the synthesis and crystallographic properties of ternary silicides $RE_6Ni_2Si_3$ with $RE = La, Ce, Pr,$ or Nd .¹ Considering this work, the compounds $RE_6Ni_2Si_3$ adopted a hexagonal structure (space group $P6_3/m$), where the sites $6h$ are occupied by a statistical mixture of nickel and silicon ($0.333Ni + 0.667Si$). Moreover, the existence of $Nd_6Ni_2Si_3$ was confirmed after annealing at 670 K.² But, recent studies report that the composition $RE_6Ni_2Si_3$ could not exist as a single phase.^{3–5} For instance, the microprobe analysis performed on the $Ce_6Ni_2Si_3$ alloy revealed that after melting, the product contains mainly the new ternary silicide $Ce_6Ni_{5/3}Si_3$, whereas the presence of $Ce_5Ni_{1.85}Si_3$ was detected

after annealing at 1073 K.⁴ Similar ternary compounds based on light rare earth elements were reported as $La_6Ni_{1.54}Si_3$ and $La_5Ni_{1.75}Si_3$,³ $Pr_6Ni_{1.57}Si_3$, $Pr_6Ni_{1.76}Si_3$, and $Pr_5Ni_{1.9}Si_3$,^{6,7} and $Nd_6Ni_{1.66}Si_3$.⁵ On the other hand, no similar ternary silicides based on rare earth elements heavier than neodymium has been evidenced to date.

More recently, we reported the existence of a ternary silicide based on cobalt $Gd_6Co_{5/3}Si_3$ that orders ferromagnetically at 294 K,⁸ a Curie temperature comparable to that observed for pure gadolinium, and is isotypic to $La_6Ni_{1.54}Si_3$ or $Nd_6Ni_{1.66}Si_3$. Moreover, our extended study synthesizes new ternary compounds $RE_6Co_{5/3}Si_3$ with $RE = Ce, Nd,$ and Tb .^{4,9} Now, by considering these results, we succeeded in preparing a new ternary silicide $Gd_6Ni_{5/3}Si_3$. We present and discuss here its crystallographic and magnetic properties. The magnetocaloric properties of $Gd_6Ni_{5/3}Si_3$ and its parent compound $Gd_6Co_{5/3}Si_3$ were investigated. They were com-

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Table 1. Crystallographic Data and Structure Refinement for $Gd_6Ni_{5/3}Si_3$

formula	$Gd_6Ni_{5/3}Si_3$
crystal color	metallic
MW (g mol ⁻¹)	1125.6
space group	$P6_3/m$
params ^a	$a = 11.7433(1) \text{ \AA}, c = 4.1857(1) \text{ \AA}$
$V (\text{\AA}^3)$	499.9(2)
Z	2
density calcd (g cm ⁻³)	7.48
crystal shape	block
temp (K)	298
diffractometer	Enraf-Nonius Kappa CCD
monochromator	oriented graphite
radiation	Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$)
scan mode	φ -scan + ω -scan
hkl range	$-17 < h < 19, -20 < k < 17,$ $-7 < l < 7$
$\theta_{\min}, \theta_{\max}$ (deg)	5, 40
linear absorption coeff	42.55 mm ⁻¹
absorption correction	Gaussian
T_{\min}/T_{\max}	0.203/0.498
no. of reflns	8879
R_{int}	0.073
no. of independent reflns	1132
reflns used ($I > 2\sigma(I)$)	953
refinement	F^2
$F(000)$	945
R factors	$R(F)/wR(F^2) = 0.032/0.075$
no. of refined params	27
GOF	1.06
weighting scheme	$w = 1/(\sigma^2(I) + 0.0016I^2)$
diff. Fourier residues (e ⁻ /\AA ³)	[-2.31, +2.38]

^a Deduced from X-ray powder diffraction.

pared with those previously reported for promising materials in magnetic refrigeration such as $Gd_5Si_2Ge_2$.¹⁰

Experimental Procedures

The polycrystalline $Gd_6Ni_{5/3}Si_3$ sample was synthesized by arc-melting a stoichiometric mixture of pure elements (purity: 99% for Gd and 99.9% for Ni and Si) in a high purity argon atmosphere. Then, the sample was turned over and remelted several times to ensure homogeneity. The weight loss during the arc-melting process was less than 0.5 wt %. Annealing was performed for 1 month at 1073 K by enclosing the sample in an evacuated quartz tube. No attack of the quartz tube by the sample and vice versa was observed.

The composition as well as the homogeneity of the annealed sample of $Gd_6Ni_{5/3}Si_3$ was checked by microprobe analysis using a Cameca SX-100 instrument. The analysis was performed on the basis of intensity measurements of Gd $L\alpha_1$, Ni $K\alpha_1$, and Si $K\alpha_1$ X-ray emission lines, which were compared to those obtained for the equiatomic ternary silicide $GdNiSi$ used as a reference compound.

X-ray powder diffraction with the use of a Philips 1050 diffractometer (Cu $K\alpha$ radiation) was applied, before and after annealing, for the characterization of the structural type and the phase identification of the samples. The electron diffraction investigation was carried out on a JEOL 2200FS microscope, operating at 200 kV, equipped with a double tilt specimen stage. Prior to the observation, the annealed sample of $Gd_6Ni_{5/3}Si_3$ was crushed in an agate mortar with alcohol. A drop of the suspension was deposited on a carbon supported grid.

Suitable single crystals of $Gd_6Ni_{5/3}Si_3$ were found in the annealed sample and selected by optical microscopy. Reflection data were collected on an Enraf-Nonius Kappa CCD area detector diffracto-

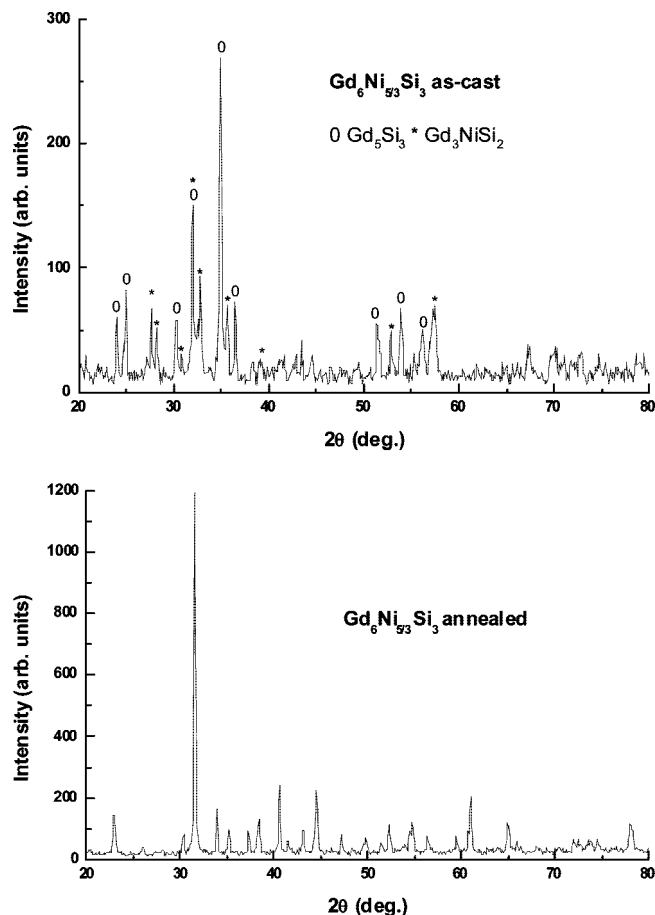


Figure 1. X-ray powder patterns of the $Gd_6Ni_{5/3}Si_3$ sample obtained by melting (as-cast) or annealing at 1073 K (O and asterisk indicate, respectively, the peak positions for Gd_5Si_3 and Gd_3NiSi_2).

meter at room temperature using Mo $K\alpha$ radiation. A Gaussian-type absorption correction was applied, the shape of the crystal being determined with the video microscope of the diffractometer. Data processing and all refinements were performed with the Jana2000 program package.¹¹ Details of the data collections and structure refinements are listed in Table 1. Other single crystals were studied to confirm that a strong disorder still is observed for nickel atoms in this compound.

Magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 4.2–470 K and applied fields up to 5 T. The heat capacity was determined with a standard relaxation method using a QD PPMS device. Samples of approximately 10 mg were glued to the sample holder using Apiezon N-grease. The heat capacity of the sample holder and grease was measured just before each sample was studied.

Results and Discussion

Existence of Phase and Crystal Structure. The analysis of the $Gd_6Ni_{5/3}Si_3$ as-cast sample by X-ray powder diffraction revealed the presence of two phases (Figure 1): the binary Gd_5Si_3 ¹² and the ternary Gd_3NiSi_2 ¹³ silicides. On the contrary, the X-ray powder pattern obtained from the annealed

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$\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ annealed

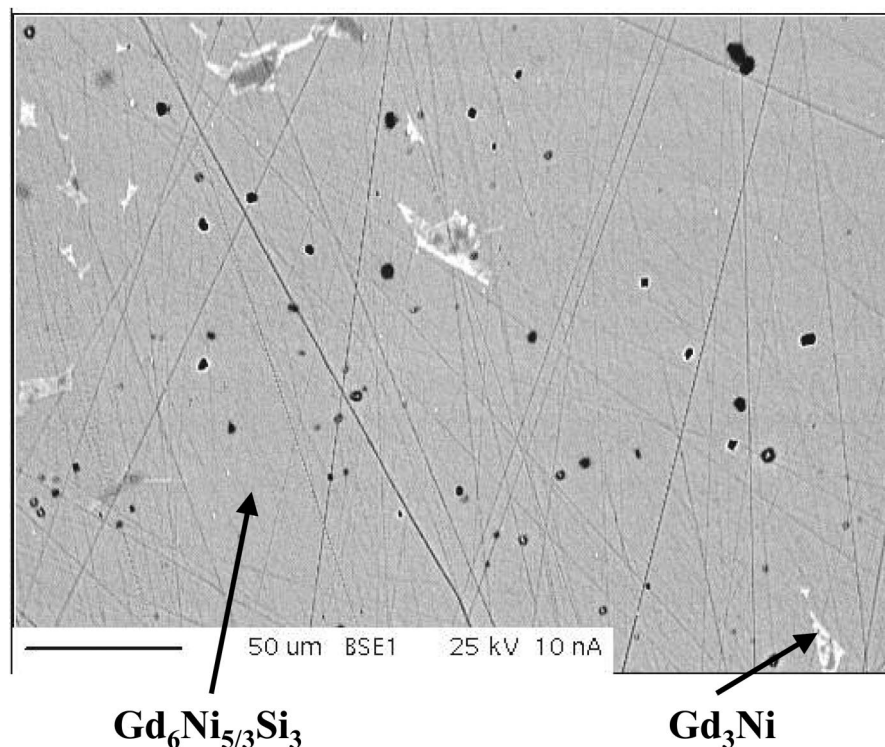


Figure 2. Microstructure of the $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ annealed sample. The main phase $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ (gray) and impurity Gd_3Ni (white) are indicated (black portions correspond to opened porosities).

sample (Figure 1) is completely indexed on the basis of a hexagonal unit cell having $a = 11.7433(1)$ Å and $c = 4.1857(1)$ Å as parameters, which are close to those reported for $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$ ($a = 11.7787$ Å and $c = 4.1640$ Å).⁸ This result suggests that the new ternary silicide $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ can be obtained as a single phase only after annealing. The microprobe analysis performed on the annealed sample confirmed this observation. The characteristic microstructure (back-scattered image) presented in Figure 2 reveals a main phase (gray) having Gd 56.3(3)%, Ni 15.3(3)%, and Si 28.4(4)% as experimental atomic percentages close to those expected for an ideal $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ stoichiometry (Gd 56.3%, Ni 15.6%, and Si 28.1%) and some amounts of the impurity Gd_3Ni (white).

From the electron diffraction experiment realized on $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$, an electron diffraction pattern with the characteristic 6-fold symmetry was obtained (Figure 3c). Then, the symmetry of the structure can only be hexagonal or cubic. This latter symmetry can be ruled out since no pattern with a 4-fold symmetry was obtained after the tilt of the specimen. Considering then the hexagonal symmetry, the value of the a -parameter (≈ 11.7 Å) can be deduced from Figure 3c. The value of the c -parameter can be calculated from Figure 3a; it corresponds to $c \approx 4.1$ Å. Furthermore, no systematic extinction was observed on this $[0-10]$ -zone axis; the extinction symbols $P-c$ - and $P-cc$ can then be excluded. Figure 3b confirms the value of the unit cell parameters. It is worthwhile to note the absence of any diffuse scattering in the electron diffraction patterns, indicating that the structure of this ternary compound has no defect.

The chemical composition determined by microprobe analysis and crystallographic properties of $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ deduced from the electron diffraction investigation suggest that this ternary silicide adopts — like $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$ — a hexagonal $\text{Ho}_4\text{Co}_{3-07}$ (or $\text{Ho}_6\text{Co}_{4-61}$)-type structure ($P6_3/m$ space group).¹⁴

The structure of $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ was refined in the space group $P6_3/m$ at room temperature and at 120 K. Both structures are very similar, and only the refinement of the room temperature XRD data will be detailed. The starting atomic positions were those of the aristotype compound $\text{Ce}_6\text{Ni}_{5/3}\text{Si}_3$.⁴ In the first step of the refinement, only the Ni2 position was introduced with a full occupancy. At this stage, high residues were observed in the difference Fourier maps within the chain of face-shared octahedra of Gd atoms (Gd1 position). As shown in the left part of Figure 4, a complete delocalization of the electron density was observed along the chain. The same behavior was observed for the low temperature 120 K measurement (right part of Figure 4). To describe this delocalization, two nonfully occupied Ni positions, Ni1 and Ni3, were introduced (Table 2). In the final stage of the refinement, the anisotropic atomic displacement parameters (ADP) were used for all positions except for these two last Ni positions. All details concerning this refinement and the atomic positions are given in Tables 1 and 2, respectively. The sum of the occupancy of the Ni1 and Ni3 atoms has been constrained to fit the expected stoichiometry. If the occupancy factors are refined for both positions, the overall

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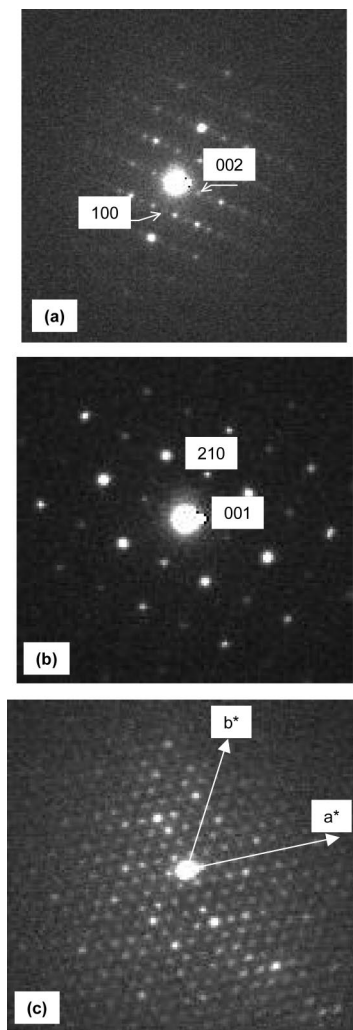


Figure 3. Electron diffraction patterns of $Gd_6Ni_{5/3}Si_3$ along the (a) [0–10], (b) [1–20], and (c) [001] directions.

formulas deduced from the refinements are $Gd_6Ni_{1.72(3)}Si_3$ and $Gd_6Ni_{1.70(3)}Si_3$ for the room and low temperature data refinement, respectively. These compositions agree with that determined by microprobe analysis.

A projection of the structure of $Gd_6Ni_{5/3}Si_3$ along the c -axis is displayed in Figure 5. The structure is made of chains of face-shared trigonal prisms of Gd atoms. In these chains, the Si and the Ni atoms (Ni2 position) occupy the center of the trigonal prisms. The $NiGd_3$ chains are surrounded by three $SiGd_3$ chains, and the $NiGd_6$ trigonal prisms share their faces with the $SiGd_6$ prisms, leading to the existence of triangular columns of four chains of face-shared trigonal prisms (Figure 5). These triangular columns are connected together through a chain of face-shared octahedra of gadolinium (Gd1 position). As previously observed by several authors,^{3–5} a perfect ordering is observed between Ni and Si atoms in the chains of trigonal prisms, whereas a delocalization of the electron density is observed in the chain of the face-shared octahedra of gadolinium. To describe this delocalization, two Ni positions usually are used:^{3–5} the Ni1 position in the center of the $[RE1_6]$ octahedra (RE1 = rare earth in the position corresponding to Gd1 in our refinement) or slightly shifted away from the center and Ni3 in the shared-face of the $[RE1_6]$ octahedra. In the case of Gd_6-

$Ni_{5/3}Si_3$, the delocalization is so strong that it has been necessary to split the Ni3 position away from the center of the face (Table 2 and Figure 5). This strong delocalization still is observed at low temperatures, and this means that this is not a dynamic but a statistical disorder. It appears that in this structural type, there is a geometric frustration caused by the value of the c -axis. Indeed, this last value is found in the range of 4.38–4.18 Å for the $RE_6Ni_{5/3}Si_3$ series (RE = La, Ce, Nd, or Gd). This means that in the present case ($Gd_6Ni_{5/3}Si_3$), if two Ni atoms occupy the center of two adjacent $[Gd1_6]$ octahedra, the distance between the two Ni1 positions would be equal to 2.093 Å. This distance is not compatible with the sum of metallic radius of nickel, which is equal to 2.492 Å.¹⁵ Then, if the centers of two adjacent octahedra are filled by Ni atoms they must be shifted away from the ideal Ni1 position to increase the Ni–Ni distance, and this induces the fact that the next octahedra cannot be filled (see ref 8 for detailed explanation). By using this approach, we have shown that the ideal stoichiometry for these phases is $RE_6Ni_{5/3}Si_3$ ^{4,8,9} as proposed by Lemaire et al. for the binary compounds $RE_6Co_{4.67}$.¹⁴ This too short c -axis and the fact that the Ni atoms are stable in the face and the center of the $[Gd1_6]$ octahedra explain the strong delocalization of the Ni atoms along the c -axis. Because of the geometric frustration, we can suppose that in each $Gd1_3$ chain, the Ni atoms are well-ordered but that the projection of all the configurations into one induces the strong delocalization observed for the Ni atoms. This geometric frustration explains why no superstructure was evidenced by electron diffraction. Indeed, whatever superstructure was imagined, the distance between the center of the two adjacent octahedra still will be too short.

As reported previously, $Gd_6Ni_{5/3}Si_3$ was not observed after fusion of the elements; at this stage, the alloy is a mixture containing mainly the two silicides Gd_5Si_3 and Gd_3NiSi_2 . In this context, it is interesting to compare the structural properties of these two last compounds to those determined presently for $Gd_6Ni_{5/3}Si_3$. In Gd_3NiSi_2 , all the Ni and Si atoms also are located in trigonal prisms $[Gd_6]$ of Gd atoms.¹³ These prisms are not all oriented in the same direction, and as pointed out by Klepp et al., no other ternary compound based on rare earth elements is known to have such a structure. Gd_5Si_3 crystallizes with the Mn_5Si_3 structure type, where the Si position is in a trigonal prismatic site formed by Gd atoms.¹² The main feature of this structural Gd_5Si_3 type is the existence of infinite chains of face-shared octahedra of Gd atoms running along the c -axis. These chains are closely related to the ones observed in $Gd_6Ni_{5/3}Si_3$ with, however, two main differences. The first difference is that these chains are empty, and the second difference is the fact that the c -value is higher (6.421 Å). It has been shown that it is possible to insert carbon or boron atoms in these chains of Gd_5Si_3 , leading to the existence of the new compounds $Gd_5Si_3C^{16}$ and $Gd_5Si_3B_{0.64}$.¹² In this last ternary boride, no delocalization of the B atoms was observed, and this can be

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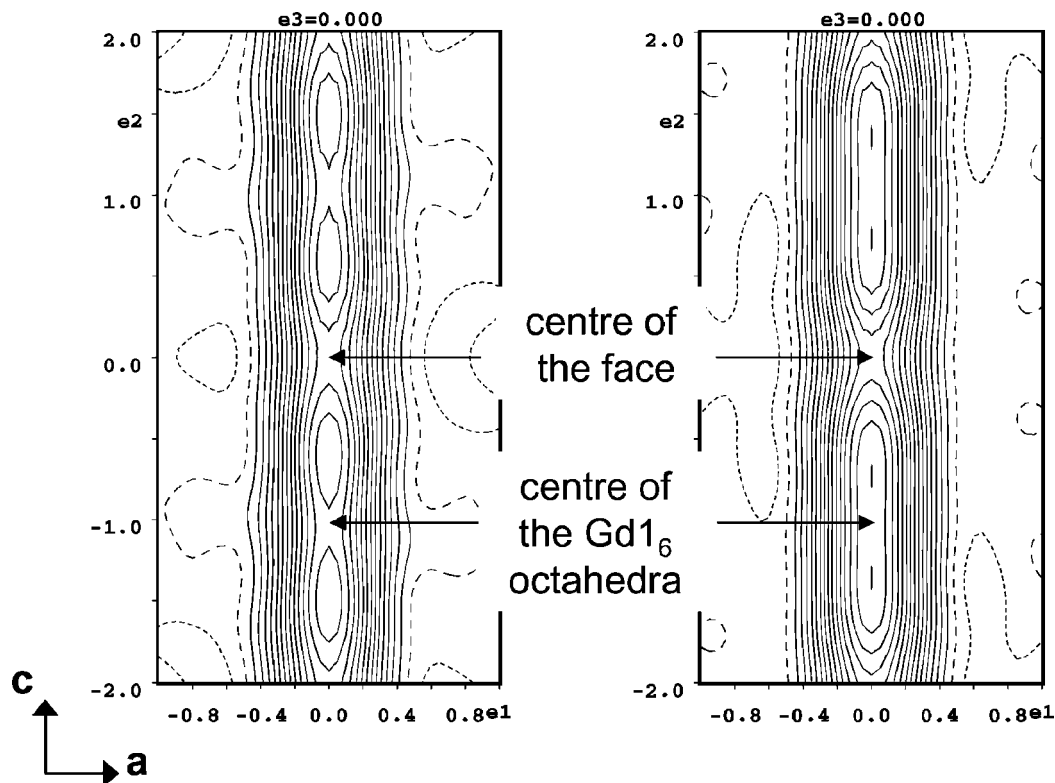


Figure 4. xz -Section at $y = 0$ of the difference Fourier maps along the chain of face-shared octahedra of gadolinium atoms. The centers of the $Gd1_6$ and face-shared octahedra are shown. The maps were calculated after the XRD refinement before the introduction of the Ni1 and Ni3 positions at (left) room temperature and (right) 120 K. Contour lines are at $-2 e^{-\text{\AA}^{-3}}$ (dashed lines) and from $+2$ to $+26$ or $+30 e^{-\text{\AA}^{-3}}$ (continuous lines) in intervals of $2 e^{-\text{\AA}^{-3}}$.

Table 2. Atomic Coordinates and Atomic Displacement Parameters for $Gd_6Ni_{5/3}Si_3$

atom	site	occupancy	X	Y	Z	U_{iso}
Gd1	6h	1	0.24123(3)	0.22910(3)	1/4	0.01117(11)
Gd2	6h	1	0.51832(3)	0.13923(3)	1/4	0.00824(10)
Ni1	4e	0.158(7)	0	0	0.062(2)	0.011(2)
Ni2	2c	1	1/3	2/3	1/4	0.0099(3)
Ni3	4e	0.176	0	0	0.315(2)	0.013(2)
Si	6h	1	0.1575(2)	0.4405(2)	1/4	0.0096(6)

related to the high value of 3.207 \AA of the B–B distance between two adjacent octahedra.

The structural properties of the two ternary silicides $Gd_6Co_{5/3}Si_3$ and $Gd_6Ni_{5/3}Si_3$ are derived from that reported for the binary compound $Gd_6Co_{4.61}$ (or $Gd_4Co_{3.07}$),¹⁴ but a similar intermetallic based on nickel does not exist; in other words, the addition of silicon to gadolinium and nickel allows us to stabilize a ternary compound having close structural properties. Also, the unit cell volume $V = 499.9 \text{ \AA}^3$ of $Gd_6Ni_{5/3}Si_3$ is smaller than that determined ($V = 500.3 \text{ \AA}^3$) for $Gd_6Co_{5/3}Si_3$,⁸ this agrees with the evolution of the metallic radius from nickel ($r_{Ni} = 1.246 \text{ \AA}$) to cobalt ($r_{Co} = 1.252 \text{ \AA}$).¹⁵ Another fact concerns the evolution of the unit cell parameters in the sequence $Gd_6Ni_{5/3}Si_3 \rightarrow Gd_6Co_{5/3}Si_3$: the a -parameter increases (+0.3%), whereas the c -parameter decreases more strongly (−0.5%). Similar behavior was evidenced for the sequence $GdNi_{0.4}Si_{1.6} \rightarrow GdCo_{0.4}Si_{1.6}$ as a increases (+0.4%) and c decreases (−0.3%); the crystal structure of these last ternary silicides also is described by stacking along the c -axis of the $[Gd_6]$ trigonal prism where

the Ni or Co and Si atoms are located.¹⁷ In other words, in these two families of compounds, the $[Gd_6]$ trigonal prisms containing the Co atom are much more compressed than those surrounding the Ni atom; this is connected to the higher decrease of the c -parameter.

If one considers the network of Gd atoms in both ternary silicides, it appears that Gd1 is located in a distorted trigonal prism of Gd1 and Gd2 with four Gd1–Gd1 distances equal to 3.467 and 3.449 \AA and two distances Gd1–Gd2 equal to 3.611 and 3.610 \AA in $Gd_6Ni_{5/3}Si_3$ (Table 3) and $Gd_6Co_{5/3}Si_3$, respectively. These trigonal prisms form by sharing faces infinite chains running along the c -axis and are surrounded by two Gd2 atoms with average distances of 3.911 and 3.964 \AA , respectively. In $Gd_6Ni_{5/3}Si_3$ and $Gd_6Co_{5/3}Si_3$, the Gd2 atoms also are located in trigonal prisms of Gd1 and Gd2 with average Gd–Gd distances of 3.636 (Table 3) and 3.641 \AA , and they are surrounded by two Gd1 atoms with average Gd2–Gd1 distances of 3.911 and 3.964 \AA , respectively. The trigonal prisms where Gd2 atoms are located form infinite chains running along the c -axis by sharing edges. These Gd–Gd distances are very similar to those observed in metallic gadolinium.¹⁸ In this metal, Gd atoms are located in regular trigonal prisms with a Gd–Gd distance of 3.573 \AA and are surrounded by six extra gadolinium atoms with Gd–Gd distances of 3.636 \AA .

Magnetic and Magnetocaloric Properties. Figure 6 presents the temperature dependence of the magnetization M of $Gd_6Ni_{5/3}Si_3$ for an applied field of 0.05 T . The main

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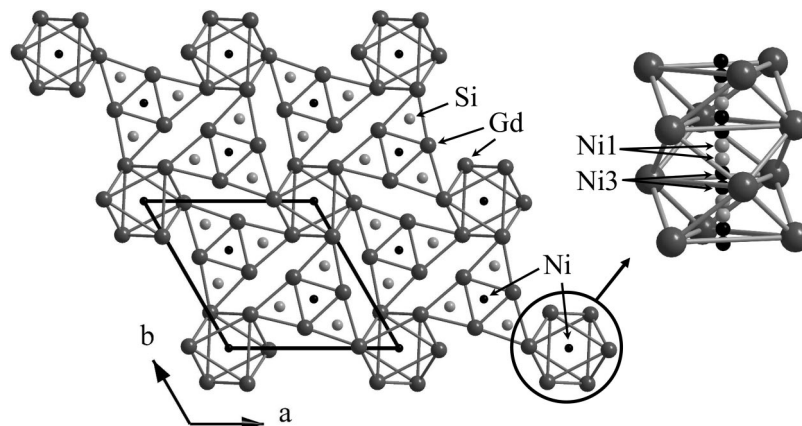


Figure 5. Projection along the c -axis of the structure of $Gd_6Ni_{5/3}Si_3$. The existence of Gd_6 trigonal prisms and octahedra is emphasized by the drawing of the Gd – Gd bonds.

Table 3. Selected Interatomic Distances (Å) in $Gd_6Ni_{5/3}Si_3$ at Room Temperature

Gd1	Ni3 ($\times 2$)	2.7777(9)
	Ni1 ($\times 2$)	2.874(2)
	Si ($\times 2$)	2.962(2)
	Si	3.094(3)
Gd2	Ni1 ($\times 2$)	3.057(4)
	Ni2 ($\times 2$)	2.9393(2)
	Si ($\times 2$)	3.061(3)
	Si ($\times 2$)	3.100(3)
Gd1	Si	3.186(2)
	Gd1 ($\times 4$)	3.4672(5)
	Gd2 ($\times 2$)	3.6108(4)
Gd2	Gd2 ($\times 2$)	3.5748(5)
	Gd1 ($\times 2$)	3.6108(4)
	Gd2 ($\times 2$)	3.7217(4)

feature of its evolution is the sharp increase in the magnetization at the Curie temperature $T_C = 310$ K (using the $M = f(H)$ curves presented in Figure 7, this temperature was determined from linear M^2 vs H/M behavior (Arrott's plots), which is predicted by the Landau theory of second order phase transition¹⁹). Also, this T_C temperature is higher than those reported, respectively, for the similar ternary silicide $Gd_6Co_{5/3}Si_3$ ($T_C = 294$ K)⁸ and pure gadolinium ($T_C = 294$ K).²⁰ This behavior led us to believe that these compounds are potentially interesting for magnetic refrigeration.

Above 320 K, the reciprocal magnetic susceptibility χ_m^{-1} of $Gd_6Ni_{5/3}Si_3$, measured with an applied field of 3 T (inset of Figure 6), follows the Curie–Weiss law. The experimental value of the effective magnetic moment $\mu_{\text{eff}} = 8.02 \mu_B/\text{Gd}$ is close to the calculated value for a free Gd^{3+} ion ($7.94 \mu_B/\text{Gd}$). This μ_{eff} value suggests that Ni is nonmagnetic in the ternary silicide. The paramagnetic Curie temperature θ_p was found to be 318 K. Such a large positive value of θ_p agrees with the ferromagnetic character of $Gd_6Ni_{5/3}Si_3$.

At various temperatures, the field dependence of the magnetization for $Gd_6Ni_{5/3}Si_3$ was measured with decreasing magnetic field (Figure 7). Below $T_C = 310$ K, these data do not reveal a remanence phenomenon. This behavior agrees with the isotropic character of the Gd^{3+} ion. Isothermal magnetization performed at low temperatures, for instance,

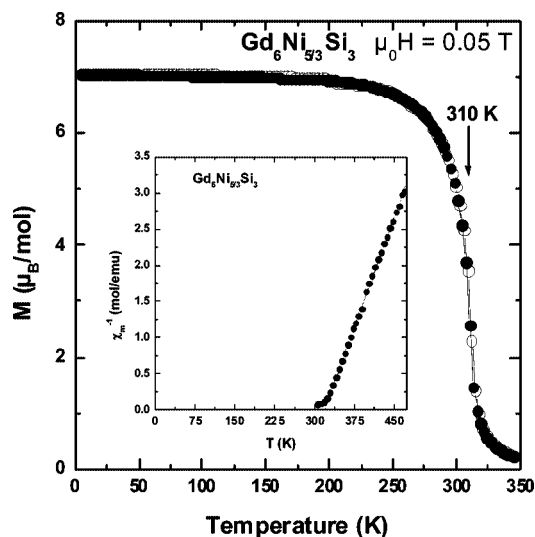


Figure 6. Temperature dependence of the magnetization M of $Gd_6Ni_{5/3}Si_3$ measured with an applied field of 0.05 T. The inset presents its reciprocal magnetic susceptibility χ_m^{-1} vs temperature (the dashed line shows the Curie–Weiss law).

at 10 or 50 K, saturates at 4.8 T with $7.10 \mu_B$ as the saturation magnetic moment per Gd atom, only slightly higher than the theoretically calculated free Gd^{3+} ion value ($7 \mu_B$). A similar excess in the saturation moment was previously reported for the silicides $(Gd_xTb_{5-x})Si_4$,²¹ 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 the magnetization just above T_C , for instance, in the 310–335 K range, does not vary linearly with the applied magnetic field. This observation indicates the existence of short-range magnetic correlations above T_C .

Using the magnetization data $M = f(H)$ (Figure 7), we calculated the isothermal magnetic entropy $\Delta S_m(T, \Delta H)$ with the Maxwell relation $\Delta S_m(T, \Delta H) = \int_{H_0}^{H_2} [\partial M(T, H)/\partial T]_H dH$.²⁰ The obtained results for applied magnetic fields H of 2 and 4.8 T are plotted for the two ternary silicides $Gd_6Ni_{5/3}Si_3$ and $Gd_6Co_{5/3}Si_3$ in Figure 8. All the curves present a single peak, in agreement with the occurrence of the

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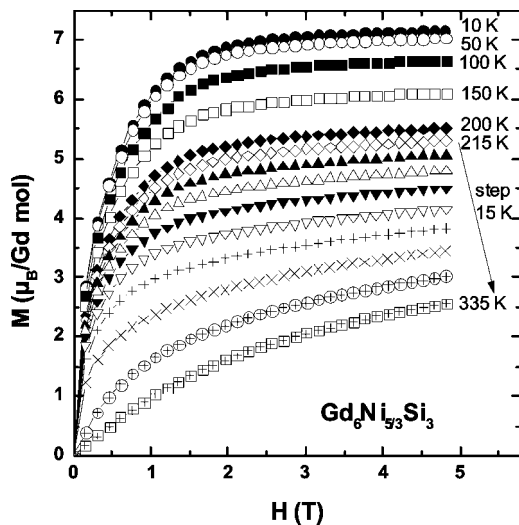


Figure 7. Field dependence of the magnetization M of $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ at various temperatures.

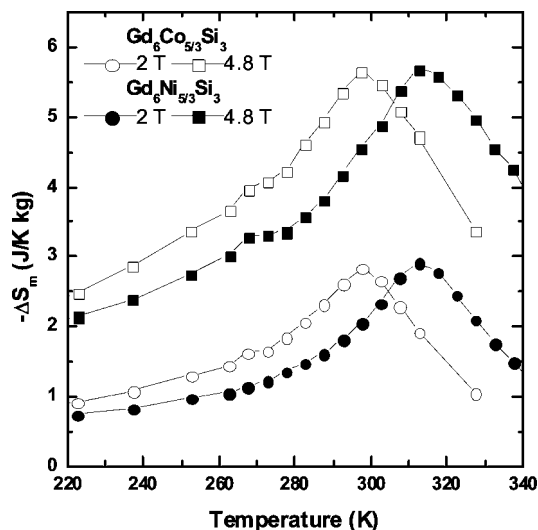


Figure 8. Temperature dependence at $H = 2$ and 4.8 T of the isothermal magnetic entropy change ΔS_m for $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ and $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$.

magnetocaloric effect, at temperatures slightly higher than the Curie temperature T_C (for $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$, ΔS_m is a maximum at 312 K, whereas $T_C = 310$ K). Moreover, the maximum of ΔS_m takes values of -2.93 J/K kg and -5.72 J/K kg for $H = 2$ and 4.8 T, respectively, for $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$. Comparable ΔS_m values were observed for the ternary silicide based on cobalt.

To determine the adiabatic temperature change ΔT_{ad} , we measured, between 2 and 375 K, the heat capacity C_p without an applied magnetic field for both ternary compounds (Figure 9). Below 200 K, the C_p curves versus temperature are practically superposed. Above this temperature, the most important feature is the well-defined λ -type anomaly signaling the ferromagnetic transition (inset of Figure 9). The order temperature is associated with the inflection point above the maximum, 292 and 310 K for $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$ and $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$, respectively, in excellent agreement with data obtained from magnetization measurements. The tails above T_C confirm the existence of short-range magnetic correlations in both compounds.

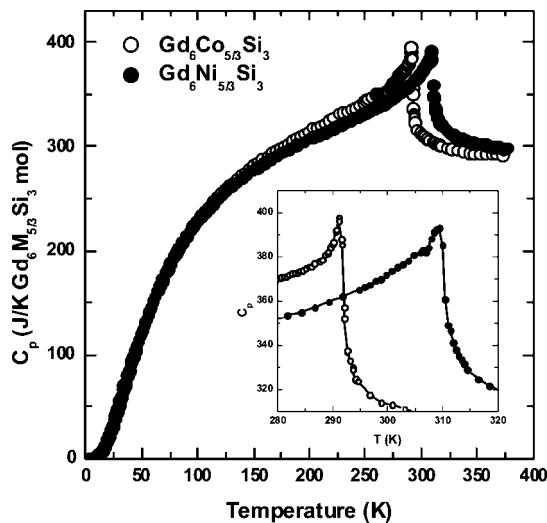


Figure 9. Temperature dependence without applied magnetic field of the specific heat C_p for $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ and $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$. Inset shows the magnetic transitions in better detail.

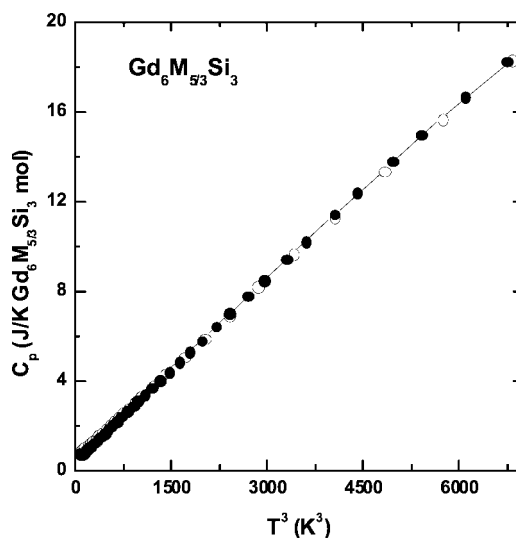


Figure 10. Specific heat C_p data as a function of T^3 for $\text{Gd}_6\text{Ni}_{5/3}\text{Si}_3$ and $\text{Gd}_6\text{Co}_{5/3}\text{Si}_3$. The continuous line is a guide for the eye.

In the low temperature range, it has been shown recently that the heat capacity of magnetic materials is well-described by a single power function of absolute temperature (T^n) for $T \rightarrow 0$.²² In the present case, we found that the exponent n that better fits the C_p values is $n = 3$, as it is shown in Figure 10, where C_p for the two ternary silicides is plotted as a function of T^3 . In Figure 10, it is observed that this power function holds up to ~ 18 K, with a similar prefactor of the T^3 function for both compounds. A similar exponent was observed in other magnetic materials, such as GdMg .²² This result indicates that the lattice heat capacity prevails and that the magnetic part of the heat capacity is contained in the prefactor of the T^3 function.²² Therefore, the Debye temperature obtained from this prefactor ($\theta_D = 198$ K) must be considered as the lower limit. In fact, this value is lower

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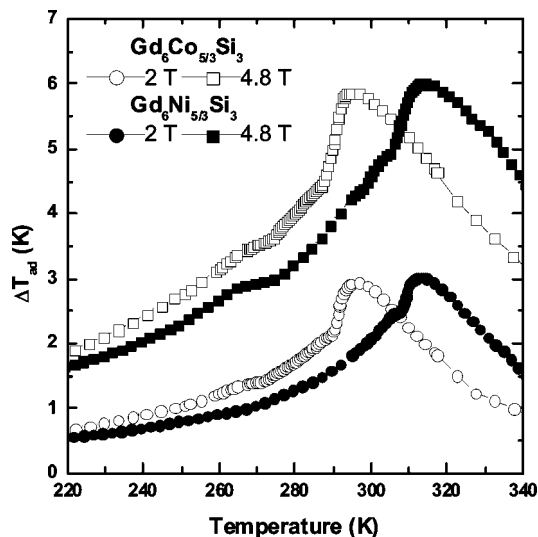


Figure 11. Temperature dependence at 2 and 4.8 T applied magnetic fields of the adiabatic temperature change ΔT_{ad} for $Gd_6Ni_{5/3}Si_3$ and $Gd_6Co_{5/3}Si_3$.

than that found for other alloys based on gadolinium, such as $GdMg$ ($\theta_D = 228$ K)²³ or $Gd_5Si_2Ge_2$ ($\theta_D = 250$ K).²⁴

The absence of a nonmagnetic isomorphous compound makes it difficult to determine the magnetic contribution C_{mag} . However, it is possible to estimate it by using a linear electronic contribution and a Debye function to model the phonon contribution in the full temperature range.²⁵ Using this procedure with a tentative Debye temperature ($\theta_D = 228$ K) and a typical electronic coefficient $\gamma = 14$ mJ/K² mol,²³ both compatible with our experimental data, we estimated $C_{mag} \approx 132$ J/K mol at the maximum of the λ peak. Therefore, as we have six Gd^{3+} ions per formula, the value corresponding to each one would be $C_{mag}/Gd^{3+} \approx 22$ J/K mol. This value is in good agreement with that predicted for simple ferromagnetic structures ($C_{mag}/Gd^{3+} \approx 20.15$ J/K mol) using a mean-field model.²⁶

Combining the heat capacity at zero field (Figure 9) and the magnetization data (Figure 7), it is possible to determine the adiabatic temperature change ΔT_{ad} . Among the different procedures to determine ΔT_{ad} , we used the one described by Pecharsky and Gschneidner²⁷ as the simplest and, simultaneously, most precise. First, from C_p data, we determined the total entropy at zero field $S(T, H = 0) = \int (C_p/T) dT$, then using the curves of the isothermal magnetic entropy $\Delta S_m(T, \Delta H)$, obtained previously from the magne-

tization data (Figure 8), we calculated the curves $S(T, \Delta H) = S(T, H = 0) + \Delta S_m(T, \Delta H)$. Once the entropy curves for the different applied fields $S(T, \Delta H)$ were obtained, we followed the standard procedure $\Delta T_{ad}(T, \Delta H) = [T(S, \Delta H) - T(S, H = 0)]_s$.²⁷ At the magnetic transition and for 2 and 4.8 T as applied magnetic fields, ΔT_{ad} was, respectively, equal to 3.1 and 6.1 K/mol for $Gd_6Ni_{5/3}Si_3$ (Figure 11). Comparable values were observed for the other ternary silicide $Gd_6Co_{5/3}Si_3$.

At this stage, it is interesting to compare the magnetocaloric properties of $Gd_6M_{5/3}Si_3$ ($M = Co$ or Ni) compounds to those reported for the different potential magnetic refrigerants: (i) ΔS_m values (-2.93 J/K kg for 2 T and $Gd_6Ni_{5/3}Si_3$) determined here for the two ternary silicides are smaller than that reported for Gd (-5.1 J/K kg for 2 T) or $Gd_5(Si_2Ge_2)$ (-14.1 J/K kg for 2 T),¹⁰ but (ii) these values of ΔS_m are comparable to those observed for other intermetallics based on gadolinium as Gd_7Pd_3 (-2.5 J/K kg for 2 T), which presents a ferromagnetic transition at 318 K.²⁸ This comparison led us to improve the magnetocaloric properties of these ternary silicides. For instance, the synthesis and characterization of substituted materials (other rare earth elements for Gd and germanium for Si) are in progress. As such, we hoped to increase the magnetocaloric properties of $Gd_6M_{5/3}Si_3$ ($M = Co$ or Ni) compounds by using during their syntheses a purer Gd metal. It was reported that the purity of the Gd metal influences strongly these properties. For instance, a $Gd_5Si_2Ge_2$ sample prepared with low purity (99%) commercial Gd metal presents an isothermal magnetic entropy ΔS_m of 7.25 J/K kg for $H = 5$ T,²⁹ which is smaller than that determined ($\Delta S_m \approx 18.5$ J/K kg for $H = 5$ T) for this compound prepared from a high purity (99.9%) Gd metal.¹⁰

Conclusion

The ternary silicide $Gd_6Ni_{5/3}Si_3$, which was obtained as single phase after annealing at 1073 K, presents an interesting ferromagnetic ordering at 310 K. This behavior is associated with a magnetocaloric effect comparable to that observed for $Gd_6Co_{5/3}Si_3$ or Gd_7Pd_3 . This suggests an interesting future study devoted to the magnetocaloric properties of the other members of this family $RE_6Ni_{5/3}Si_3$, where $RE = Pr, Nd, \dots$ etc.

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Supporting Information Available: XRD data for $Gd_6Ni_{5/3}Si_3$ at 120 K (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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