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Bernard Chevalier, Etienne Gaudin, François Weill. The new ternary silicides RE₆Co_{1.67}Si₃ (RE = Ce, Nd, Gd, Tb, Dy) investigated by X-ray diffraction and magnetization measurements. *Journal of Alloys and Compounds*, 2007, 442 (1-2), pp.149-151. 10.1016/j.jallcom.2006.06.111 . hal-00159492

HAL Id: hal-00159492

<https://hal.science/hal-00159492>

Submitted on 3 Jul 2007

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**The new ternary silicides $RE_6Co_{1.67}Si_3$ (RE = Ce, Nd, Gd, Tb, Dy) investigated by X-ray diffraction
and magnetization measurements**

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Abstract

These compounds crystallize in the hexagonal structure (space group $P6_3/m$) related to the $Gd_6Co_{1.67}Si_3$ -type. The magnetization measurements reveal that: (i) the cerium exhibits a trivalent state in $Ce_6Co_{1.67}Si_3$ but no magnetic ordering is evidenced above 1.8 K; (ii) on the contrary, two ferro(ferri)magnetic transitions are detected for $Nd_6Co_{1.67}Si_3$ (84 K and 35 K) and $Tb_6Co_{1.67}Si_3$ (183 K and 39 K); in both case, a remanence phenomena appears for temperatures below the higher magnetic transition; (iii) similar behavior does not exist for $Gd_6Co_{1.67}Si_3$ which shows only one ferromagnetic transition below $T_C = 294$ K. The occurrence of a complex magnetic phase diagram for $Nd_6Co_{1.67}Si_3$ and $Tb_6Co_{1.67}Si_3$ can be correlated to the existence of two crystallographic sites for rare earth atoms in this new family of compounds.

PACS: 61.66.Fn; 75.25.+z

Keywords: Intermetallics; Magnetisation

1. Introduction

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The first member of this family, $\text{Gd}_6\text{Co}_{1.67}\text{Si}_3$, was discovered by us as impurity phase in GdCoSi alloys [1]. It presents an interesting ferromagnetic transition ($T_C = 294(2)$ K) close to room temperature, which could be associated with a magnetocaloric effect. $\text{Gd}_6\text{Co}_{1.67}\text{Si}_3$ crystallizes with the hexagonal " $\text{Ce}_6\text{Ni}_2\text{Si}_3$ " structure type (space group $P6_3/m$). As previously evidenced by Lemaire *et al.* [2] and Prots' *et al.* [3, 4] for homologous compounds $\text{Gd}_4\text{Co}_{4.61}$, $\text{La}_6\text{Ni}_{1.54}\text{Si}_3$ and $\text{Nd}_6\text{Ni}_{1.66}\text{Si}_3$, these phases are non-stoichiometric and the overall formula should be written $\text{Ce}_6\text{Ni}_{2.8}\text{Si}_3$. Using X-ray powder or single crystal diffraction, an ordered distribution between Co and Si was found in $\text{Gd}_6\text{Co}_{1.67}\text{Si}_3$ and $\text{Ce}_6\text{Co}_{1.67}\text{Si}_3$ [1, 5], one site being not fully occupied by Co for steric reasons. Moreover, two different kinds of environments are observed for rare earth (RE) atoms. The first one, RE_1 is surrounded by 3 Si, 10 RE and 3 Co. The partial occupation of the later position induces a disordered surrounding for RE_1 position. The second one, the RE_2 position is surrounded by 2 Co, 5 Si and 10 RE. Now, we have extended the study to similar ternary silicides based on other rare earth. We present and discuss here on their synthesis, crystal structure and magnetic properties.

2. Experimental

Polycrystalline $\text{RE}_6\text{Co}_{1.67}\text{Si}_3$ samples were synthesized by arc-melting a stoichiometric mixture of the pure elements (purity above 99.9%) in a high purity argon atmosphere. Then, the samples were 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 done for one month at 1073 K by enclosing the samples in an evacuated quartz tube.

The composition as well as the homogeneity of the annealed samples have been checked by microprobe analysis. The analysis was performed on the basis of intensity measurements of RE- $L_{\alpha 1}$, Co- $K_{\alpha 1}$ and Si- $K_{\alpha 1}$ x-ray emission lines, which were compared with those obtained for RECo_2Si_2 used as reference compounds. The phase identification of the samples have been done, before and after annealing, by means of X-ray powder diffraction (Cu- $K\alpha$ radiation). The unit cell parameters were determined by a least-squares refinement method using silicon (5N) as an internal standard. Magnetization measurements were performed using a Superconducting QUantum Interference Device (SQUID) magnetometer in the temperature range 1.8-370 K and applied fields up to 5 T.

3. Results and discussion

Microprobe and X-ray diffraction analysis show that the compounds $RE_6Co_{1.67}Si_3$ with $RE = Ce, Nd$ and Gd are obtained as single phase after melting of the constituents. On the contrary, an annealing under vacuum at 1073 K for one month is necessary in order to prepare $Tb_6Co_{1.67}Si_3$. Indeed after melting this alloy is a mixture containing mainly $TbCoSi$ and Tb_5Si_3 . Finally, $Dy_6Co_{1.67}Si_3$ exists but it is not obtained as single phase after similar annealing. In other words, the thermal stability of these compounds is dependent to the nature of the rare earth element. All the $RE_6Co_{1.67}Si_3$ compounds crystallize in the hexagonal structure related to the $Gd_6Co_{1.67}Si_3$ -type [1]. Their unit cell parameters decrease with the size of RE (Table 1). No anomaly can be observed for the unit cell parameters of $Ce_6Co_{1.67}Si_3$ which suggests that the cerium is trivalent in this ternary silicide. From $Ce_6Co_{1.67}Si_3$ to $Tb_6Co_{1.67}Si_3$, the a -parameter which is governed by the Co-Si sublattice, decreases (2.9 %) less than the c -parameter (3.4 %) influenced by the size of the RE^{3+} ions.

Above 80 K, the temperature dependence of the reciprocal magnetic susceptibility χ_m^{-1} of $Ce_6Co_{1.67}Si_3$ shows Curie-Weiss behavior with an experimental magnetic moment of $2.59 \mu_B/Ce$ atom, close to the free ion value of $2.54 \mu_B$ for Ce^{3+} . At lower temperatures than 80 K, the $\chi_m^{-1} = f(T)$ curve deviates from a straight-line behavior, presumably due to thermal depopulation of crystal-field levels. The large negative paramagnetic Curie temperature $\theta_p = -77$ K, determined by linear extrapolation of the $\chi_m^{-1} = f(T)$ plot to $\chi_m^{-1} = 0$, is indicative of a Kondo compound. No magnetic ordering is evident down to 1.8 K.

The magnetization of $Nd_6Co_{1.67}Si_3$ has been measured and the results are reported in Fig. 1 (inset highlights the behavior of its reciprocal susceptibility in the high-temperature region). This ternary silicide perfectly follows, above 120 K, a Curie-Weiss law $\chi_m^{-1} = (T - \theta_p)/C_m$ with positive $\theta_p = 78$ K and $C_m = 9.81 \text{ emu K mol}^{-1}$ giving an effective moment $\mu_{\text{eff}} = 3.61 \mu_B/Nd$ atom (Table 1) very close to the value expected for a free Nd^{3+} ion ($\mu_{\text{eff}} = 3.62 \mu_B$). This result indicates that Co is non-magnetic in the ternary silicide. At low temperatures, the magnetization M of $Nd_6Co_{1.67}Si_3$ is strongly dependent of its cooling history. In Fig. 1 is shown the thermal dependence of its magnetization cooled in zero field (ZFC curve) and after cooling in an applied field $\mu_0H = 0.05$ T (FC curve). A strong irreversibility between the

ZFC and FC branches appears below $T_C = 84$ K. The ZFC curve exhibits a maximum at $T_t = 35$ K and a strong decrease around $T_C = 84$ K (temperature defined by a minimum in the derivative curve dM_{ZFC}/dT). On the contrary, with decreasing temperatures, two sharply increases near T_C and T_t are observed in the FC curve. These results suggest the existence of two magnetic transitions for $Nd_6Co_{1.67}Si_3$. The field dependence of its magnetization (not presented here) reveals: (i) the existence of remanence increasing with decreasing temperature below $T_C = 84$ K; for instance, the remanence is equal to $0.98 \mu_B/Nd$ atom at 6 K; (ii) a tendency to saturate with increasing field below T_C ; at 6 K and for $\mu_0H = 5$ T, the saturation magnetic moment is equal to $1.93 \mu_B/Nd$ atom. This last value is clearly smaller than that calculated for a free Nd^{3+} ion ($3.27 \mu_B$). Two explanations can be proposed: (i) the low value of the moment could be due to quenching of the angular momentum by the crystalline electric field or (ii) the occurrence of different moments on the two inequivalent sites of Nd atoms in this ternary silicide. This investigation reveals that $Nd_6Co_{1.67}Si_3$ exhibits two magnetic transitions: one having ferro or ferrimagnetic character below $T_C = 84$ K in agreement with the positive value of the paramagnetic Curie temperature $\theta_p = 78$ K and the second near 35 K corresponding probably to a spin reorientation.

Above 220 K, the magnetic susceptibility of $Tb_6Co_{1.67}Si_3$ follows a Curie-Weiss law with an effective experimental magnetic moment $\mu_{eff} = 9.30 \mu_B/Tb$ atom weakly smaller than the theoretical value ($9.72 \mu_B$) ascribed to Tb^{3+} free ion (Table 1). Like $Nd_6Co_{1.67}Si_3$, this compound presents a positive paramagnetic Curie temperature $\theta_p = 183$ K. Also, two magnetic transitions are evidenced from the $M = f(T)$ curves obtained by the ZFC and FC modes (Fig. 2) : a ferro or ferrimagnetic ordering appears below $T_C = 183$ K and another is detected near $T_t = 39$ K (at this temperature the FC curve exhibits a maximum). Also for $Tb_6Co_{1.67}Si_3$ an irreversibility between the ZFC and FC branches appears below $T_C = 183$ K. The measurement of M versus field shows the existence of remanence ($2.62 \mu_B/Tb$ at 6 K) and saturation moment ($4.70 \mu_B/Tb$ at 6 K and $\mu_0H = 5$ T) smaller than that expected for Tb^{3+} free ion saturated moment ($9 \mu_B$). This behavior is comparable to that reported presently on $Nd_6Co_{1.67}Si_3$. As can be seen in Fig. 2, the ZFC curve for $Tb_6Co_{1.67}Si_3$ starts at very low negative values for temperatures smaller than 9 K. Usually, negative magnetization appears in complex ferri- or canted antiferromagnetic systems. For instance, similar behaviour was reported recently on $TbFe_{3.5}Al_{8.5}$ single crystal [6]. The negative magnetization was ascribed to the occurrence of a large coercivity at low temperatures in conjunction with an unbalance of magnetic domains.

The magnetic properties of the $\text{RE}_6\text{Co}_{1.67}\text{Si}_3$ ternary silicides result from the indirect exchange interaction between the $4f(\text{RE})$ moments via conduction electrons. In this model proposed by Ruderman, Kittel, Kasuya and Yosida [7-9], the ordering temperature (T_C) is proportional to the de Gennes factor $G = (g_J - 1)^2 J(J+1)$ where g_J is the Landé factor and J the total angular momentum of the RE^{3+} ion [10]. Considering the G factor and $T_C = 294$ K the ordering temperature of $\text{Gd}_6\text{Co}_{1.67}\text{Si}_3$, we estimate 196 and 34 K as T_C temperature respectively for $\text{Tb}_6\text{Co}_{1.67}\text{Si}_3$ and $\text{Nd}_6\text{Co}_{1.67}\text{Si}_3$. The calculated T_C value for $\text{Tb}_6\text{Co}_{1.67}\text{Si}_3$ is in agreement with the experimental one. On the contrary, a strong difference is observed for $\text{Nd}_6\text{Co}_{1.67}\text{Si}_3$; this suggests that the crystalline-electric-field (CEF) plays an important role on the magnetic properties of this last ternary silicide.

4. Conclusion

The preliminary study concerning the $\text{RE}_6\text{Co}_{1.67}\text{Si}_3$ compounds indicates complex magnetic properties for $\text{Nd}_6\text{Co}_{1.67}\text{Si}_3$ and $\text{Tb}_6\text{Co}_{1.67}\text{Si}_3$. These properties are certainly linked to the existence of two inequivalent Nd or Tb atom in their crystal structure. Neutron powder diffraction is in progress in order to determine the two magnetic transitions appearing at T_C and T_t temperatures for these ternary silicides.

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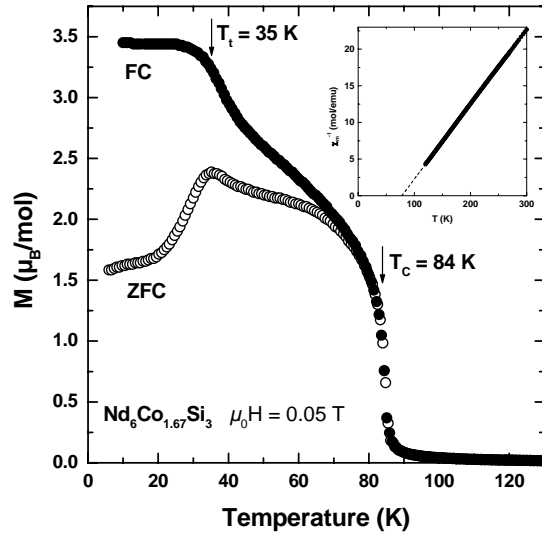


Fig. 1. Temperature dependence at $\mu_0 H = 0.05$ T of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of $\text{Nd}_6\text{Co}_{1.67}\text{Si}_3$. Inset presents the reciprocal magnetic susceptibility χ_m^{-1} versus temperature for $\text{Nd}_6\text{Co}_{1.67}\text{Si}_3$ at $\mu_0 H = 4$ T. The dashed line corresponds to the Curie-Weiss fit.

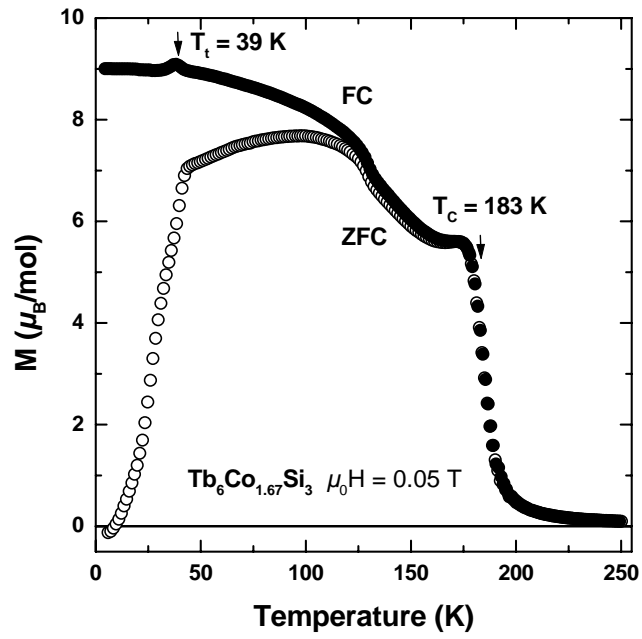


Fig. 2. Temperature dependence at $\mu_0 H = 0.05$ T of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of $\text{Tb}_6\text{Co}_{1.67}\text{Si}_3$.

Table 1

Crystallographic and magnetic data relative to RE₆Co_{1.67}Si₃ silicides

Compound	Crystallographic data		Magnetic data				Reference
	<i>a</i> (Å)	<i>c</i> (Å)	μ_{eff} (μ_{B}/RE)	θ_{p} (K)	T_{C} (K)	T_1 (K)	
Ce ₆ Co _{1.67} Si ₃	12.039	4.2624	2.59	-77			*
Nd ₆ Co _{1.67} Si ₃	11.931	4.2503	3.61	78	84	35	*
Gd ₆ Co _{1.67} Si ₃	11.7787	4.1640			294		[1]
Tb ₆ Co _{1.67} Si ₃	11.685	4.118	9.30	183	183	39	*

* this work