Magnetic structures of the ternary silicide Nd$_6$Ni$_{1.67}$Si$_3$

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Abstract.
The ternary silicides RE$_6$T$_{1.67}$Si$_3$ (RE = Ce, Pr, Nd, Gd, Tb and T = Co, Ni) crystallizing with the hexagonal Ce$_6$Ni$_{1.67}$Si$_3$-type structure has been recently extensively studied. It has been shown that some of these compounds exhibit interesting magnetocaloric properties. In this work, the magnetic structures of the Nd$_6$Ni$_{1.67}$Si$_3$ compound were determined by means of neutron powder diffraction. According to previous magnetization and specific heat measurements, this compound exhibits two successive magnetic transitions at 84 K and 38 K. The first transition corresponds to a ferromagnetic arrangement of the Nd-moments along the c-axis and the second one to a non-collinear ferromagnetic arrangement yielding a conical structure. The magnetic structures of Nd$_6$Ni$_{1.67}$Si$_3$ are compared to those of the Nd$_6$Co$_{1.67}$Si$_3$ homologous ternary silicide.

1. Introduction
Recently, a new series of compounds with the general formula RE$_6$Co$_{1.67}$Si$_3$ (RE = Rare-Earth) was discovered [1, 2]. These compounds crystallize with the hexagonal Ce$_6$Ni$_{1.67}$Si$_3$ aristotype structure [3]. Homologous compounds with nickel instead of cobalt were studied in the past and more recently [3–6]. To compare the properties of both series with cobalt and nickel, compounds with gadolinium or neodymium as RE were chosen. In the case of Gd$_6$M$_{1.67}$Si$_3$ (M = Co, Ni) compounds, a ferromagnetic behaviour is observed for both silicides around room temperature, with $T_C = 294$ K for Gd$_6$Co$_{1.67}$Si$_3$ and 310 K for Gd$_6$Ni$_{1.67}$Si$_3$. They exhibit interesting and similar magnetocaloric properties [6–8] with a same adiabatic temperature change, e.g. $\Delta T_{ad} = 3.1$ K for $\Delta H = 2T$ [6]. The magnetic properties of Nd$_6$Co$_{1.67}$Si$_3$ and Nd$_6$Ni$_{1.67}$Si$_3$ compounds were also compared and it has been shown that a ferro- or ferrimagnetic transition is observed at 84 K for both [9]. Below this magnetic transition a second one was observed at $T' = 38$ and 35 K for Nd$_6$Ni$_{1.67}$Si$_3$ and Nd$_6$Co$_{1.67}$Si$_3$, respectively. The comparison of the temperature dependence of their magnetization M(T) showed significant differences below 40 K. To characterize the two magnetic transitions, neutron diffraction experiments were carried out and the results obtained for Nd$_6$Ni$_{1.67}$Si$_3$ will be presented in this paper.

2. Experimental details
The polycrystalline Nd$_6$Ni$_{1.67}$Si$_3$ sample was synthesized according to the procedure detailed previously in [9].
Neutron powder diffraction experiment was performed at the Orphee reactor (CEA/Saclay, France) on the two-axis diffractometer G4.1 ($\lambda = 2.423$ Å; 800 cell-position-sensitive detector). Several patterns were recorded between 1.5 and 100K. The data were analysed using the Rietveld profile method by means of the Fullprof program [10].

3. Results and discussion
The neutron powder diffraction patterns recorded at 100, 40 and 1.5K on the Nd$_6$Ni$_{1.67}$Si$_3$ sample are shown in Figure 1 as well as the difference diagram 1.5 - 40K. At 100K, above $T_C = 84K$, the peaks are only of nuclear origin and can be indexed with the space group $P6_3/m$ as expected.

![Figure 1. Selected neutron diffraction patterns of Nd$_6$Ni$_{1.67}$Si$_3$. The ticks correspond to 2$\theta$-Bragg positions for (1) the nuclear phase, (2) the magnetic phase associated to $\vec{k} = (0 0 0)$ and (3) the magnetic phase associated to $\vec{k} = (1/3 1/3 0)$.

Between 100 and 80K, some nuclear peaks start to grow up indicating the occurrence of a ferro- or ferrimagnetic ordering in agreement with the magnetization measurements and no additional peaks appear with decreasing temperature down to 40K (Figure 1). Thus, the magnetic peaks are indexed with the propagation vector $\vec{k} = (0 0 0)$ between 40K and $T_C$ which means that the magnetic structure may be described within the nuclear unit cell over the whole temperature range. The magnetic atoms, i.e. only the Nd1 and Nd2 atoms [9], are located in two different $6h$ sites. Symmetry analysis using magnetic group theory can provide relations between the Nd-magnetic moments of each site $6h$ (Nd1 and Nd2) in the unit cell. The Bertaut’s analysis method applied to the $P6_3/m$ space group associated to the $\vec{k} = (0 0 0)$ propagation vector, gives 6 irreducible representations (IR) for each $6h$ site. The basis vectors of IR are detailed in [11]. For each IR, the moment’s components of the atoms M4 (-x -y 3/4), M5 (y -x+y 3/4) and M6 (x-y x 3/4) are the same or opposite to those of the atoms M1 (x y 1/4), M2 (-y x-y 1/4) and M3 (-x+y -x 1/4) respectively. At 40K, i.e. just above $T' = 38K$, the best fit is obtained with the $\Gamma 1$ representation ($R_{B\text{-nucl}} = 3.9\%$ and $R_{B\text{-mag}} = 4.8\%$) and corresponds to a ferromagnetic structure with Nd-moments aligned along the c-axis. This is exactly the same structure as that determined for Nd$_6$Co$_{1.67}$Si$_3$ [11] and this is coherent with their common magnetization feature between 40 and 84K [9]. The magnetic moments values are $\mu_1 = 1.58(5) \mu_B$ and $\mu_2 = 2.48(5) \mu_B$ for Nd1 and Nd2 atoms at 40K, respectively.
Below 40K, the magnetic contribution under the nuclear peaks is saturated whereas some small additional peaks appear in the neutron diffraction patterns (Figure 1). They are characteristic of the occurrence of an additional magnetic component. These peaks can be indexed with the propagation vector \( \overrightarrow{k} = (1/3 1/3 0) \). The Bertaut’s analysis method associated to this \( \overrightarrow{k} \) gives the same 6 IR as those mentioned above for \( \overrightarrow{k} = 0 \). But in this case, each \( 6h \) site is split in two orbits O1 and O2 containing (M1, M2, M3) and (M4, M5, M6) respectively. This means that, according to group theory, the parameters of one IR for O1 are not linked to those for O2.

At 1.5K, the only good fit associated with \( \overrightarrow{k} = (1/3 1/3 0) \) is obtained with a planar spiral model (\( R_B = 13.3 \% \)). This structure is depicted in Figure 2. In each orbit, magnetic moments include an angle of 120°, and they are tilted at 120° with respect to the propagation vector direction according to the magnetic cell period. Along the \( \overrightarrow{k} \) direction, the moments of the atoms located in the plane \( z = 1/4 \) (dashed red line on Figure 2) turn in the opposite sense of those located in the plane \( z = 3/4 \) (full black line). Taking into account the ferromagnetic component along the \( c \)-axis and the cycloidal one in the basal plane, the magnetic structure of Nd\(_6\)Ni\(_{1.67}\)Si\(_3\) is thus a conical structure. At 1.5K, the magnetic moments amount to \( \mu_1 = 2.28(10) \) and \( \mu_2 = 2.72(11) \mu_B \) for Nd1 and Nd2 atoms respectively and the cone angles (angle between the Nd-moment and the \( c \)-axis) are \( \theta_1 = 48(3)° \) and \( \theta_2 = 19(4)° \). As previously observed for Nd\(_6\)Co\(_{1.67}\)Si\(_3\), \( \mu_2 \) is higher than \( \mu_1 \) and both values are lower than the value of the free Nd\(^{3+}\)-ion (3.27 \( \mu_B \)). This is probably due to the crystal field effect; in particular, the Nd1-atom around the disordered chain of Ni \([9]\) may explain the partial quenching of \( \mu_1 \). The presence of a zero resulting component into the basal plane may explain the occurrence of the metamagnetic transition at fields around 2.6T observed in the M(H) curve at 6K \([9]\).

The temperature dependence of the \( \mu_1 \) and \( \mu_2 \) moments are depicted in Figure 3 as well as the cone angles \( \theta_1 \) and \( \theta_2 \). It shows that both Nd sublattices order at the same temperature around 85K. \( \mu_2(T) \) exhibits an usual behavior with the temperature whereas an anomaly is observed in the \( \mu_1(T) \) curve: \( \mu_1 \) seems to saturate around 40K, then increases again below 40K in the conical structure. Moreover, below 40K, \( \theta_1(T) \) and \( \theta_2(T) \) saturate rapidly and reach different values: \( \theta_1 = 48(3)° \) and \( \theta_2 = 19(4)° \) at 1.5K.

It is noteworthy that the magnetic structures of Nd\(_6\)Ni\(_{1.67}\)Si\(_3\) and Nd\(_6\)Co\(_{1.67}\)Si\(_3\) are similar above 40K but differ below this temperature. Indeed, below 40K in Nd\(_6\)Co\(_{1.67}\)Si\(_3\), the Nd-moments have a common ferromagnetic component parallel to \( c \)-axis and components within the \((a, b)\) plane at 60° and 120° from each other. This magnetic arrangement induces a resulting ferromagnetic component within the \((a, b)\) plane \([11]\). On the contrary, in Nd\(_6\)Ni\(_{1.67}\)Si\(_3\) the spiral arrangement of the moments’component in the \((a, b)\) plane leads to a resulting component which is equal to zero. That explains the difference of behavior in the M(T) curves for both silicides.

![Figure 2. Projection of the magnetic structure of Nd\(_6\)Ni\(_{1.67}\)Si\(_3\) into the basal plane \((a, b)\). Four nuclear cells are represented.](image-url)
Figure 3. Temperature dependence of the magnetic moments values ($\mu_1, \mu_2$) and cone angles ($\theta_1, \theta_2$) for Nd1 and Nd2.

when the temperature decreases, the occurrence of a resulting ferromagnetic component into the $(a, b)$ plane induces an increase of the magnetization at 38 K for Nd$_6$Co$_{1.67}$Si$_3$ (FC curve). Whereas, for Nd$_6$Ni$_{1.67}$Si$_3$, the occurrence of a zero resulting component into the $(a, b)$ plane at 38 K induces a maximum in the magnetization curve (FC curve).

4. Conclusion

Thanks to the neutron powder diffraction study, the difference of magnetic behavior between Nd$_6$Ni$_{1.67}$Si$_3$ and Nd$_6$Co$_{1.67}$Si$_3$ is now better understood. This difference is correlated to a different magnetic ordering in the basal plane $(a, b)$ at low temperature. For Nd$_6$Ni$_{1.67}$Si$_3$ the arrangement of the moment’s component is cycloidal in this plane and this explains the slight decrease of the magnetization below the low temperature transition at 38 K. To extend the magnetic characterization of Nd$_6$Ni$_{1.67}$Si$_3$ neutron diffraction studies under different applied fields need to be carried out. This will help to understand the original evolution of the magnetization versus field previously observed [9].

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