Single crystal growth and magnetic characterization of $R\text{NiSi}_3$ ($R = \text{Dy}, \text{Ho}$)

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Abstract
We have investigated the structural and magnetic properties of the new intermetallic compounds $R\text{NiSi}_3$ ($R = \text{Dy}, \text{Ho}$) grown by the Sn-flux method, which yields high quality single crystals. X-ray powder diffraction data show that these compounds crystallize in a layered orthorhombic structure ($\text{SmNiGe}_3$-type). Temperature dependent magnetization between 2 K and 310 K is anisotropic and reveals that the ground states are antiferromagnetic. Low-temperature magnetic isotherms up to $H = 70$ kOe exhibit multiple metamagnetic transitions and alternating reversible–irreversible regions in the ordered state, which are dependent on temperature, magnetic field and crystal orientation. From this complex magnetic behavior we have built tentative magnetic phase diagrams for the two compounds.

Keywords: magnetic anisotropy, metamagnetism, rare earth nickel silicides, single crystals

1 Introduction
Complex anisotropic magnetic properties are exhibited at low temperatures in some compounds of the intermetallic family $RTX_3$, where $R$ is a rare earth element, $T$ is a transition metal and $X$ is Si or Ge. The $R\text{NiGe}_3$ series, for example, exhibits antiferromagnetic (AFM) ground states, metamagnetic transitions in most of the compounds and a strong anisotropy due to crystal electric field (CEF) effects [1]. In particular, the compound CeNiGe$_3$, that has been studied in the last decade, was classified as an antiferromagnetic Kondo lattice [2, 3], with its low-temperature physical properties strongly dependent on the magnetic field [4], and a superconductor state below 0.48 K and under pressure [5].

In contrast, little is known about the $R\text{NiSi}_3$ series. The first and only reported synthesis for most members of this series was in a 1977 work by Gorelenko et al.[6], where the authors obtained polycrystals and found simple paramagnetic behaviors at high temperatures (between 80 K and 1200 K).

The first comprehensive characterization of any member was performed in 2004 for single crystals of YbNiSi$_3$ [7], that was established as an AFM Kondo lattice with a Néel temperature
of 5.1 K. Later works described the magnetic phase diagram for YbNiSi$_3$\[8\] and reported a suppression of the magnetic order when replacing Si with Ge\[9\]. A thorough search for quantum critical behavior in this compound was reported in ref. \[10\] and a full magnetic characterization was described in ref. \[11\], where neutron scattering technique was used to determine the magnetic structure. For other members, only a detailed crystallographic characterization of singlecrystalline ErNiSi$_3$ was described in a 2005 work \[12\], where it was also determined that this compound crystallizes in the orthorhombic space group $Cmmm$ and that it adopts the SmNiGe$_3$ structure type.

Here we report the first successful flux-growths of DyNiSi$_3$ and HoNiSi$_3$ single crystals, and present a preliminary crystallographic and magnetic characterization using X-ray powder diffraction, plus temperature and field dependent magnetization curves. Both compounds have revealed surprisingly complex magnetic behavior at low temperatures, which are summarized in tentative magnetic phase diagrams.

2 Experimental methods

Single crystals of DyNiSi$_3$ and HoNiSi$_3$ were grown using the Sn-flux method \[13, 14\] starting with a R:Ni:Si:Sn molar proportion of 1:1:3:45. All elements were supplied by Alfa Aesar with purities of 99.9% for Dy and Ho, 99.95% for Ni and 99.999% for Si and Sn. The elemental reagents were sealed directly in evacuated quartz ampoules and melted at 1200°C in a box furnace during 10 hours. The resulting liquid was cooled down over 150 hours to 500°C and then centrifuged to separate the crystals from the remaining flux. The final samples were cleaned in HCl during 30 minutes to remove eventual flux droplets from the crystal surfaces.

X-ray powder diffraction was conducted in a Stoe diffractometer, model STADI P, with Cu K$_\alpha$ radiation and at room temperature. The magnetic characterization of the samples was conducted in a SQUID-VSM from Quantum Design, using a temperature range between 2 K and 310 K, and external applied fields up to 70 kOe. Due to the hysteretic magnetic behavior of the crystals, the samples were demagnetized before each measurement with an oscillating magnetic field and warmed above their Néel temperatures.

3 Results and Discussion

The flux-grown single crystals of DyNiSi$_3$ and HoNiSi$_3$ display a thin plate-like shape (see figure 1) with a main surface area up to few square millimeters and thickness of up to 0.5 mm. Similar plate-like shape was reported for the RNiGe$_3$ series \[1\] and for YbNiSi$_3$ \[7\], with the $b$ crystallographic axis perpendicular to the main surface, indicating that this series has a thin platelike crystal growth habit because the layer stacking in the $b$ direction grows at a much slower rate than the $ac$-plane growth. Rietveld refinements of the X-ray powder diffraction data (figure 1) show that both DyNiSi$_3$ and HoNiSi$_3$ crystallize in the layered orthorhombic space group $Cmmm$ of SmNiGe$_3$, as reported for the other series family members ErNiSi$_3$ \[12\] and YbNiSi$_3$ \[7\]. The refined lattice parameters values for DyNiSi$_3$ are $a = 3.915(1)$ Å, $b = 20.928(1)$ Å, and $c = 3.940(1)$ Å. For HoNiSi$_3$ the values are $a = 3.905(1)$ Å, $b = 20.889(1)$ Å, and $c = 3.926(1)$ Å. Due to the very close values of the $a$ and $c$ lattice parameters in these compounds, they can sometimes be regarded as tetragonal with respect to their physical properties, but in other cases relevant anisotropies are found in the $ac$ plane. The decrease in the lattice parameters of HoNiSi$_3$ compared to DyNiSi$_3$ is expected according to the well established lanthanide contraction of the heavier rare earth elements, as found in other intermetallic series \[1, 15\]. We also performed
Figure 1: X-ray powder diffraction for DyNiSi$_3$ and HoNiSi$_3$ single crystals. The blue lines are the experimental data and the red ones are the Rietveld refinements. The insets show pictures of the crystals used for magnetization measurements on a scale of 1 mm.

A Laue backscattering diffraction measurement on the main surface of the DyNiSi$_3$ sample, and although the diffractogram did not provide enough resolution to distinguish between the $a$- and $c$-axis of the sample, it indicated a quasi-tetragonal structure in this plane. Additionally, the results of the Rietveld refinement show that the $a$ and $c$ lattice parameters have almost the same value, but are very different from those of the $b$ lattice, so, together with the Laue pattern, we can conclude that the $b$ axis for these single crystals is indeed perpendicular to the main surface of the samples.

Some ternary intermetallic rare earth compounds show complex and anisotropic magnetic behavior, as a result of interactions such as long-range and indirect RKKY exchange, Kondo effect, and effects of the crystal electric field [16]. The compound YbNiSi$_3$, the only one of the series RNiSi$_3$ that has had its magnetic behavior well characterized [7, 8, 9, 10, 11], shows an AFM ground state below the Néel temperature $T_N = 5.1$ K, and its AFM axis is along the $b$ axis. In figure 2, we show the anisotropic magnetic properties obtained for the single crystals of DyNiSi$_3$ (figures 2a and 2b) and HoNiSi$_3$ (figures 2c and 2d).

The AFM behavior of the DyNiSi$_3$ crystal is ascertained in figure 2a, showing the temperature dependence of the inverse susceptibility ($\chi^{-1} \times T$) under an external applied field $H = 1000$ Oe, for the two directions perpendicular to the $b$ axis (closed and open circles) as well as the parallel one. The black square symbols represent the polycrystalline average $(\chi_{\perp,1} + \chi_{\perp,2} + \chi_{\parallel})/3$, and the black line is the fit at high temperatures of the Curie-Weiss law $\chi(T) = C/(T - \theta_p)$ on the average curve. These yield an effective magnetic moment of $\mu_{\text{eff}} = 10.45(3) \mu_B$, very close to that of the free ion Dy$^{3+}$ ($\mu = 10.63 \mu_B$), and a Curie-Weiss
Figure 2: Magnetization measurements for DyNiSi$_3$ (a, b), and HoNiSi$_3$ (c, d). Panels (a) and (c) show $\chi^{-1} \times T$ under $H = 1000$ Oe, aligned parallel and perpendicular to the $b$ axis. The black square symbols represent the polycrystalline average curves and the black lines are their Curie-Weiss fits at high temperatures. The open and closed circles are the experimental data perpendicular to the $b$ crystallographic axis, while the star symbols were taken parallel to the $b$ axis. The insets show $\chi \times T$ near the respective AFM transitions. Figures (b) and (d) show magnetization isotherms at $T = 2$ K with $H \parallel b$ and $H \perp b$ (at two perpendicular orientations (1) and (2)). The respective insets zoom in on multiple metamagnetic transitions that occur for $H \perp b$. The error bars are of the same size as the experimental points.

The temperature of $\theta_p = -38(1)$ K, where the negative sign indicates the antiferromagnetic coupling. The inset panel of fig. 2a presents the behavior of the $\chi \times T$ near the AFM phase transition.
and shows that, unlike YbNiSi$_3$ which has an easy axis along the $b$ direction, DyNiSi$_3$ single crystals feature an easy AFM axis within the plane orthogonal to the $b$ crystallographic axis. The Néel temperature obtained from the derivative $d(\chi T)/dT$ is $T_N = 19.0(9)$ K. The main panel of figure 2b shows the anisotropic field-dependence of the magnetization at $T = 2$ K for the $H \parallel b$ orientation, and two perpendicular $H \perp b$ orientations. The two curves with $H \perp b$ have a similar behavior, but they only attain a magnetic moment per formula unit of $7.3 \mu_B$, smaller than the free ion Dy$^{3+}$ magnetic moment, so it is possible that there is another metamagnetic transition above 7 T. The isotherm for $H \perp b$ shows a hysteretic metamagnetic transition, characterized by a step in the magnetization, with $\Delta H \approx 1700$ Oe. This type of transition can arise
in systems in which two magnetic states are separated by an energy barrier [16]. The inset graph shows several isotherms at different temperatures with $H \perp b$, where a close look reveals that the hystereses display two metamagnetic transitions, highlighting the complex magnetic behavior of this compound. The magnetization curve with $H \parallel b$ (perpendicular to the AFM alignment), shows an almost linear dependence with the applied field.

For the HoNiSi$_3$ single crystal, the same type of magnetic characterization shows that this compound also features an easy AFM axis in the plane perpendicular to the $b$ crystallographic axis (figures 2c and d), with an effective magnetic moment of $\mu_{\text{eff}} = 10.60(1) \mu_B$, perfectly consistent with that of the free ion Ho$^{+3}$ ($\mu = 10.60 \mu_B$), and a Curie-Weiss temperature of $\theta_p = -6.1(2)$ K. For this compound, we tentatively attribute a Néel temperature of $T_N = 10(1)$ K based on a visible kink in all $\chi \times T$ curves, but a strong decrease in magnetization only occurs at much lower temperatures, below 7 K. Contrary to the large hysteresis displayed by DyNiSi$_3$, HoNiSi$_3$ only shows a small hysteretic metamagnetic transition (of about 400 Oe) at 2 K. The two curves with $H \perp b$ achieve different magnetic moments between 17 kOe and 70 kOe. Curve (1) nearly reaches the value of the saturation magnetic moment of Ho$^{+3}$. The isotherms presented in the inset of figure 2d show that the magnetic behavior of this compound is also characterized by multiple metamagnetic transitions.

In order to better characterize the complex magnetic behavior of these compounds, we have built tentative phase diagrams, presented in figure 3, by carefully tracing the $T$-temperature dependence of all the main features appearing in the magnetic data. The points were obtained from the derivative of the isotherms ($dM/dH$). The isotherms are shown in the inset panels of figures 2c and 2d, and presented in figures 3a and 3b. Figure 3c displays the hysteretic magnetic behavior of the two metamagnetic transitions of DyNiSi$_3$, with two lines for each transition, corresponding to curves with ascending or descending fields. In the case of HoNiSi$_3$ (Figure 3d), the hysteresis is small, so the error bar encloses both curves. HoNiSi$_3$ presents multiple metamagnetic transitions, leading to at least seven magnetic phases, assuming that the last (upper) one separates the magnetically ordered region from the paramagnetic phase.

4 Conclusions

In this work, we have successfully grown DyNiSi$_3$ and HoNiSi$_3$ single crystals by the Sn-flux method. The crystals have a plate-like morphology, and X-ray powder diffraction showed that they belong to the orthorhombic space group $Cmmm$ of the SmNiGe$_3$-type structure. The susceptibility measurements exhibited an anisotropic behavior and an AFM ground state with Néel temperatures of $19.0(9)$ and $10(1)$ K for DyNiSi$_3$ and HoNiSi$_3$, respectively, which likely scales with the de Gennes factors for these rare earths. The magnetization versus applied field isotherms up to $H = 70$ kOe showed multiple metamagnetic transitions and alternating reversible–irreversible regions in the ordered state. Based on derivative curves of the isotherms, we have built tentative magnetic phase diagrams for those compounds, although these need a more thorough study to be resolved. Future work shall aim to grow and characterize compounds with the remaining rare earth elements, in order to explore the trends in their magnetic behavior along the series. Microscopic techniques are also being planned for better understanding of the rich behaviors presented in the magnetically ordered phases.
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References


