Experimental report

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Proposal: **5-31-2759** **Council:** 4/2020

Title: Determination of magnetic structures of RE3Fe3Sb7 (RE = Pr, Nd) usingpowder neutron diffraction

Research area: Chemistry

This proposal is a new proposal

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Samples: Pr3Fe3Sb7
Nd3Fe3Sb7

Instrument	Requested days	Allocated days	From	To
D20	3	3	08/02/2021	11/02/2021

Abstract:

The intermetallic compound Nd3Fe3Sb7 is composed of two magnetic sublattices within an Sb framework. One-dimensional strands of face sharing Fe octahedra and stacks of triangularly arranged Nd atoms propagate along c direction. Magnetization measurements indicate complex and highly temperature dependent antiferromagnetic behavior of those sublattices. For weak magnetic fields, conventional antiferromagnetic behavior disappears upon cooling below 55 K and samples display a magnetic moment antiparallel to the external field . This effect of negative magnetization even occurs by spontaneous polarization at zero field. The rare earth substitution (Pr and Sm) strongly alters magnetic properties of the compound. Elucidating the magnetic structure is indispensable to understand the complex magnetic properties by sublattice interaction of those compounds. Therefore, we propose thermal neutron powder diffraction for Nd3Fe3Sb7 and Pr3Fe3Sb7.

Experimental Report

Determination of magnetic structures of $RE_3Fe_3Sb_7$ (RE = Pr, Nd) using powder neutron diffraction

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Introduction and state of science

The crystal structure and first observation of unusual magnetic behavior of $Nd_3Fe_3Sb_7$ have been reported by Nasir et al., however, an in depth study has not been performed due to the unavailability of appropriate samples [1]. We succeeded in the synthesis of powder samples and high quality, needle-shaped crystals of $Nd_3Fe_3Sb_7$ ($P6_3/m$, a = 13.180(2) Å, c = 4.1843(7) Å at T = 293 K) and, for the first time, of isostructural $Pr_3Fe_3Sb_7$ and $Sm_3Fe_3Sb_7$ via flux growth technique. Notably the Nd and Pr compounds have been under investigation for their very unusual magnetic behaviors. Magnetization measurements show spontaneous negative magnetization at ZFC, and two distinctively different magnetic regimes at high and low temperature with reversed magnetization upon cooling. The transition region features magnetic compensation and sign reversal of the magnetization for both cooling and heating (see Figure 1). This behavior is very likely the result of two competing magnetic substructures (Fe and *RE*) as has previously been observed experimentally for variations of magnetic ordering among substructures in literature [2, 3]. The neutron data which will be discussed in the following supports this behavior and sheds light on the complex magnetic interplay in the compounds.

Experiments at ILL and results

Powder neutron diffraction experiments were performed for $Pr_3Fe_3Sb_7$ and $Nd_3Fe_3Sb_7$ on D20 diffractometer in the temperature range of 1.7 K to 400 K (Pr) and 500 K (Nd compound) which allowed determination of the spin structure in the high and low temperature regime, the transition region as well as in the paramagnetic state.

For $\mathbf{Pr_3Fe_3Sb_7}$, neutron diffraction data were recorded at the temperatures given in Table 1 (left). We found a contribution of magnetic scattering at $T \leq 350$ K which is limited exclusively to the Bragg reflections of the nuclear structure (k = (0, 0, 0)), mainly on the strong $\langle 10\bar{1}0\rangle$ and $\langle 2\bar{1}\bar{1}0\rangle$ reflection. The refinement of the magnetic structure with JANA2006 [4] shows ferromagnetic alignment of the Fe moments along the c-direction with the magnetic space group $P6_3/m$ (no. 1374) [5]. The moment increases to lower temperatures from 0.7(1) μ_B at 300 K to 1.0(1) μ_B at 70 K per Fe atom. Neutron diffraction at 20 K and 7 K reveal a contribution of the *RE* substructure with magnetic scattering now including the $\langle 3\bar{1}\bar{2}0\rangle$, $\langle 10\bar{1}1\rangle$ reflections and others (see Figure 2). Refinement of the two substructures in $P6_3/m$ gives two ferromagnetically ordered substructures that are aligned antiparallel, thus partially cancelling each other out. However, higher fit agreement is obtained by lowering the symmetry of the magnetic structure from $P6_3/m$ to $P6_3$ (no. 1360) [5]. Removing the mirror plane perpendicular to the c-direction allows for canting of the spins and thus a magnetic contribution in the ab-plane.

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[1] Nasir, N. et al., *Intermetallics* **2010**, *18*, 2361–2376.
[2] Oster, M. et al., *Chem. Mater.* **2019**, *31*, 9317–9324.
[3] Kumar, A.; Yusuf, S. M., *Phys. Rep.* **2015**, *556*, 1–34.
[4] Petříček, V. et al., *Z. Kristallogr. - Cryst. Mater.* **2014**, *229*, 345–352.
[5] Litvin, D. B., *Magnetic Group Tables: Part 2*, *IUCr*, **2013,** 2957–2958, 2988–2989.

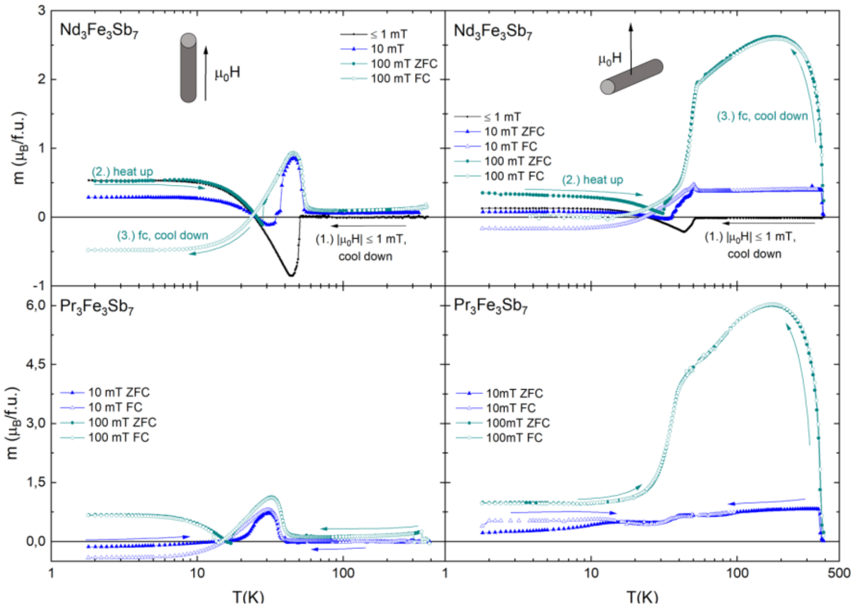

Figure 1: Field and temperature-dependent magnetic moments of $Nd_3Fe_3Sb_7$ and $Pr_3Fe_3Sb_7$.

As displayed in Figure 2 (inset), the *RE* moments rotate towards the antimony atom in the center. By *RE-TM* interaction, the Fe moments also undergo a slight tilting away from the *c*-direction. We do not see any evidence for such a behavior at elevated temperatures which indicates that the tilting is initiated when the *RE-RE* long-range order sets in, realigning the Fe moments by substructure interaction. As magnetic scattering for the contribution of the moment in *a* and *b* occurs at the same diffraction angle, powder neutron diffraction does not allow to determine a defined orientation in the *ab*-plane. Consequently, only the angular deviation from the *c*-axis is given in Table 1.

The Nd compound displays very similar behavior (Table 1, right) with slight differences in the magnetic moment on the *RE* position and different canting angles. The magnetic transitions occur at higher temperatures as expected from magnetization data. The Fe magnetic moment seems larger as compared to the Pr compound; we attribute this to a small side phase that contributes to the $\langle 10\bar{1}0\rangle$ reflection.

Table 1: Fe and RE moments per atom for $Pr_3Fe_3Sb_7$ (left) and $Nd_3Fe_3Sb_7$ (right) obtained from powder neutron diffraction. θ_{Mc} indicates the angle between the total moment and the c-axis.

<table>
<tr><th>T [K]</th><th>M_{Fe} [μ_B] | θ_{Mc} [°]</th><th>M_{Pr} [μ_B] | θ_{Mc} [°]</th><th>M_{Fe} [μ_B] | θ_{Mc} [°]</th><th>M_{Nd} [μ_B] | θ_{Mc} [°]</th></tr>
<tr><td>500</td><td></td><td></td><td>—</td><td>—</td></tr>
<tr><td>400</td><td>—</td><td>—</td><td>0.8(1) | 0</td><td>—</td></tr>
<tr><td>300</td><td>0.7(1) | 0</td><td>—</td><td>1.1(1) | 0</td><td>—</td></tr>
<tr><td>200</td><td>0.9(1) | 0</td><td>—</td><td>1.2(1) | 0</td><td>—</td></tr>
<tr><td>100</td><td></td><td></td><td>1.3(1) | 0</td><td>—</td></tr>
<tr><td>70</td><td>1.0(1) | 0</td><td>—</td><td>1.3(1) | 0</td><td>—</td></tr>
<tr><td>40</td><td></td><td></td><td>2.0(1) | 24(7)</td><td>–1.3(1) | 155(8)</td></tr>
<tr><td>20</td><td>1.5(1) | 11(5)</td><td>–1.6(1) | 145(3)</td><td></td><td></td></tr>
<tr><td>7</td><td>1.7(1) | 37(3)</td><td>–2.1(1) | 132(2)</td><td>2.1(1) | 31(5)</td><td>–2.1(1) | 164(4)</td></tr>
</table>

The neutron data is in good agreement with our magnetization experiments. Temperature dependent overview scans confirm the transition temperature from the paramagnetic to the ferromagnetic state of the Fe substructure as well as the ordering temperature of the *RE* substructure. Data recorded at 20 K for the Pr compound show an almost equal but antiparallel contribution from the two substructures. This reflects very well the magnetic compensation observed at 18 K in magnetization experiments. At 40 K, the Nd compound is in the transition region from Fe ordering only to competing substructure interaction. The neutron data illustrates very well the initial domination of the Fe magnetic substructure which is compensated at lower temperatures. At 7 K we observe that the contribution of the *RE* substructure has overcome the Fe contribution and the net magnetization becomes negative if spin rotation by 180° is hindered by e.g. magnetocrystalline anisotropy. This is also supported by the magnetization data and hysteresis loops indicating a soft magnet at high temperatures and a hard magnet at low temperatures (not shown here).

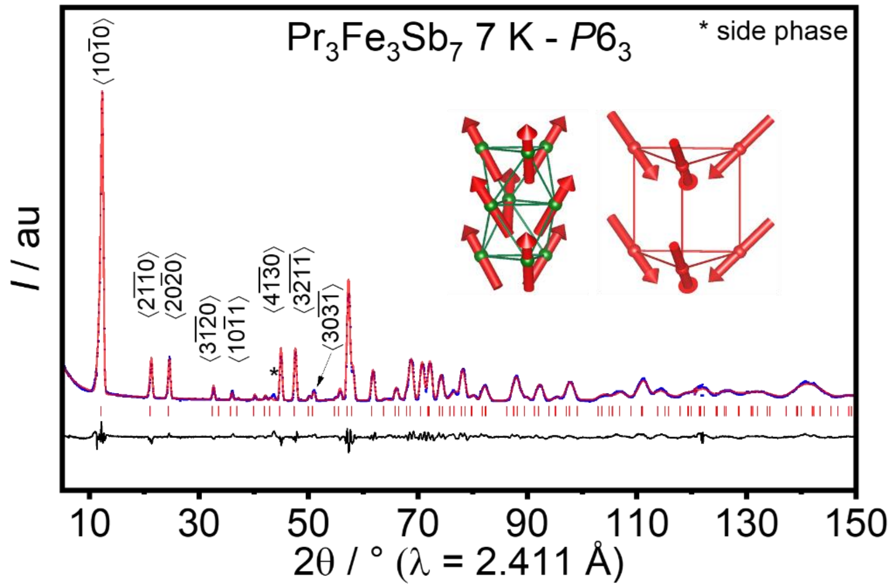

Figure 2: Neutron diffraction pattern for $Pr_3Fe_3Sb_7$ at 7 K. The inset shows canted magnetic moments of the Fe and Pr substructure.

The canted spin model preserves the magnetic compensation of M_c around 20 K and could also account for the magnetic moment that is observed in *a*- and *b*-direction (perpendicular to the needle axis) according to the magnetization experiments at weak fields (see Figure 1).

Outlook

The neutron diffraction experiments helped to obtain a fundamental understanding of the magnetic interactions in the ternary compounds. The neutron data provides helpful information about alignment of magnetic moments in the individual substructures. This understanding will be crucial in the interpretation of magnetization experiments and complementary analysis by Moessbauer spectroscopy. We hope thus to further study this complex and highly interesting behavior in magnetic fields as well.