Neutron Diffraction Study on the Magnetic Structure of Pr₆Fe₁₃Sn

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ARTICLE INFO
Article history:
Received 20 November 2009
Received in revised form 3 April 2010
Accepted 20 April 2010

Keywords:
Rare-earth intermetallics
Neutron diffraction
Antiferromagnetic
Pr₆Fe₁₃Sn

ABSTRACT
We have successfully prepared a Pr₆Fe₁₃Sn sample by employing argon arc melting. The crystal structure of the sample has been examined by an x-ray diffraction. The x-ray pattern reveals that the sample crystallize in the tetragonal Nd₆Fe₁₃Si structure type with space group I₄/mcm. Neutron diffraction at 150K performed on a powder sample shows a collinear antiferromagnetic ordering of the Fe and Pr sublattices with the wave vector (0, 0, 1) and an I₄ type magnetic lattice with anti-centering translation. The main axis of antiferromagnetism is restricted to the (0 0 1) plane. The average refined Fe moments at 150 K is (2.0±0.4) µB whereas the Pr moments are (2.1±0.4) and (1.9±0.4) µB for the 8f and 16l sites, respectively.

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INTRODUCTION
Compounds with a chemical formula RₓFe₁₃ₓ₋₄X (R=light rare-earth Pr and Nd; X=nonmetal Cu, Ag, Au, AL, Si, Ge, Sn) are frequently obtained when transition metal rich Fe-based alloys are used as starting materials for NdₓFe₁₃₋₄B or PrₓFe₁₃B type permanent magnets. It is believed that the role of the second phase of RₓFe₁₃ₓ₋₄X-type may enhance the coercivity in NdₓFe₁₃₋₄B-type permanent magnets with an X element addition. Since the NdₓFe₁₃₋₄B-type permanent is an important technology material, it is of special interest to study the structural and magnetic properties of these second phase compounds.

The crystal structure of the compounds of the composition RₓFe₁₃ₓ₋₄X₁ₓ₋₄ was unrevealed in 1985 by Siechevich et al. [1]. Particularly they have shown that compound La₀.₉Co₁₁Ga₃ orders in a tetragonal structure with space group I₄/mcm. Later on, Allemand et al. [2] have shown that NdₓFe₁₃₋₄Si crystallizes as an ordered variant of this compound. The crystal structure is rather complicated with four different Fe sites, namely 16k, 16l₁, 16l₂ and 4d, two Nd nonequivalent sites, 8f and 16l, and one Si site 4a, forming a naturally layered atomic arrangement. The R atoms, especially those at the 16l₁ site, have mainly other R atoms as nearest neighbors. Consequently, in these compounds the 4f – 4f interaction, which is normally much smaller than the 4f – 3d and 3d – 3d interaction, might be of importance [3].

A strong debate about the magnetic properties of RₓFe₁₃ₓ₋₄X has arisen. Claims about ferromagnetism [4], ferromagnetism with compensation point [5], and antiferromagnetism [6] have been made. This controversy has prompted us to prepare six RₓFe₁₃ₓ₋₄X compounds (R=Pr and Nd; X=Si, Ge and Sn) single phase as far as possible and to reexamine their magnetic behavior. The magnetic properties of the compounds our investigated by employing Cu-Kα X-ray powder diffraction, ⁵⁷Fe Mössbauer at temperatures in the range 295 – 500 K using a standard transmission spectrometer equipped with an Austin Science VF-1000 vacuum furnace. The source was ⁵⁷Co embedded in a Rh matrix. Also we employed a thermogravimetric analyzer (TGA) in a small magnetic field gradient using a Perkin Elmer TGA-7. AC-susceptibility was measured in a LakeShore Closed-cycle susceptor at 137 Hz. Néel temperatures were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7, using the heat capacity peak at Tₙ to signal ordering. We have shown that the compounds order antiferromagnetically at room temperature [7].

It should be noted that neutron diffraction experiment on PrₓFe₁₃Sn performed at temperature 1.5K was reported [8]. They reported the R atom at the 16l₁ site is weakly magnetic and its refined magnetic moment at room temperature is almost zero. Here, we present our neutron diffraction study...
of Pr$_6$Fe$_{13}$Sn compound in order to reexamine the paper of Schobinger-Papamantellos et al [8]. Our data was collected at 150 K and analyzed using GSAS [9].

This paper is organized as follows. First we describe experimental details of our sample preparation and measurement techniques. Next, we explain the successive experimental results. Finally, the main conclusions are presented.

**EXPERIMENTAL METHODS**

The Pr$_6$Fe$_{13}$Sn sample, with a weight of ~ 5 g, was prepared from high purity materials of at least 99.9% purity by arc melting in an atmosphere of purified argon. After melting, the ingot was wrapped in Ta foil, sealed in a sealed quartz tube under a partial pressure of purified argon at 973 K for one week. After annealing, the tube was quenched in water. Samples for x-ray and neutron diffraction experiments were prepared by crushing the resultant alloys under acetone using a mortar and pestle. The x-ray diffraction pattern was obtained on the high resolution diffractometer of E9 at temperature 150 K. The step increment in 2θ was 0.05° and the 2θ range from 5° to 156°. The pattern was corrected for absorption and evaluated by means of the Rietveld method using GSAS program.

**RESULTS AND DISCUSSION**

In Fig. 1 we display the x-ray diffraction patterns of Pr$_6$Fe$_{13}$Sn randomly oriented powder samples. Analyses of the x-ray pattern was accomplished via the Rietveld method using the computer code GSAS. The refinement process of the Rietveld method requires a set of initial crystal parameter values and a correct space group. We used the atomic positions and lattice constants of Nd$_6$Fe$_{13}$Sn proposed by Allemand et al. [2] to start the refinement. It can be seen on the figure the theoretical (solid lines) pattern agree well with the observed (dots) pattern. The R factors, namely $R_p=1.50$, $R_w=1.97$ and $\chi^2=7.8$, are satisfactory. Furthermore, no observed peaks unaccounted for and no extra miss fit peaks implying that the crystallographic structures of the samples confirm the Pr$_6$Fe$_{13}$Sn structure types reported previously by Allemand et al. [2]. In other words, the sample is virtually single-phase. The final refined lattice constants of Pr$_6$Fe$_{13}$Sn are $a=8.0914(8)$ Å and $c=23.4687(4)$ Å whereas the atomic positions and are presented in Table 1. Numbers in parentheses are experimental errors.

![Table 1. Refined atomic positions of Pr$_6$Fe$_{13}$Sn deduced from x-ray diffraction data.](image_url)

The magnetic structure of Pr$_6$Fe$_{13}$Sn has been investigated using powder neutron diffraction by Schobinger-Papamantellos et al. [11]. The magnetic unit cell of Pr$_6$Fe$_{13}$Sn is modeled as collinear moments of six ferromagnetic blocks. Each ferromagnetic block is embedded between two successive Sn layers perpendicular to the z axis located at $z=0.25$ and 0.75. The magnetic moments in these ferromagnetic blocks alter their sign collectively when going to the next blocks along the z axis. As shown in Fig. 2 a model of magnetic structure of Pr$_6$Fe$_{13}$Sn due to [11] was displayed.

Neutron diffraction pattern of the polycrystalline powder Pr$_6$Fe$_{13}$Sn sample collected at temperature 150 K is shown in Fig. 3. The most important feature of the patterns is the appearance of a (0 0 1) peak located at $2\theta = 3.4^\circ$. Since the diffraction condition for the space group $I4/mcm$ is $h + k + l = 2n$, the occurrence of the (0 0 1) peak indicates that the magnetic ordering of Pr$_6$Fe$_{13}$Sn is antiferromagnetic. Furthermore, the magnetic lattice of Pr$_6$Fe$_{13}$Sn is $I_0$ with a wave vector (0, 0, 1). Thus, all Fe and Pr moments related by the $I$ translation $+(1/2, 1/2, 1/2)$ are antiparallel. It should be noted that with the exception of the (0 0 1) peak, the other magnetic contributions are difficult to distinguish from the nuclear reflections due overlap. This is made the data analysis is more difficult and the refined magnetic moment values are imprecise.

Following Opechowski and Guccione [10], there are sixteen magnetic space groups in the family of the crystallographic $I4/mcm$ space group. They are presented in Table 2.
The magnetic space groups in column A can be ruled out immediately since they do not comprise \( I_p \). Moreover, the Pr-1 atom at the Wyckoff position \( 8f \) has a point symmetry group 4. The magnetic space group cannot have a \( 4' \) component since the \( 4' \) symmetry is not an admissible magnetic point group. Thus, four of the eight possible magnetic space groups in column B can be skipped. However, none of the remaining magnetic space groups permits the magnetic moment to point along the \( a \) or \( b \) axis which gives rise to the \((0 \ 0 \ 1)\) reflections.

The neutron patterns of the \( \text{Pr}_6\text{Fe}_5\text{Sn} \) collected at 150 K was analyzed by employing the magnetic structure model of \( \text{Pr}_6\text{Fe}_5\text{Sn} \) proposed by Schobinger-Papamantellos et al. [11]. Fig. 3 shows the neutron diffraction pattern of the \( \text{Pr}_6\text{Fe}_5\text{Sn} \) recorded at 150 K. The reliability factors are \( R_{w} = 9.5 \% \) and \( R_p = 7.1 \% \) and \( \chi^2 = 4.8 \). It should be emphasized here that since the magnetic contribution is weak, the refined magnetic moments are imprecise. Within experimental error, the Fe sites have not reached the saturation value of 2.0(4) \( \mu_B \) at 150 K. The respective magnetic moment values of Pr \( 8f \) and \( 16j \) sites are 2.1 (4) and 1.9 (4) \( \mu_B \). These values are below the magnetic moment of free \( \text{Pr}^{3+} \) ion value \( gJ = 3.2\mu_B \). The refined crystal constants of \( \text{Pr}_6\text{Fe}_5\text{Sn} \) at 150 K are \( a = 8.1051(2) \) Å and \( c = 23.4589(2) \) Å whereas the atomic positions and are presented in Table 3. As comparison, the refined atomic parameters at 1.5 K obtained by Schobinger-Papamantellos et al. [8] are listed in Table 4. It can be seen that the results of our neutron diffraction data and those of Schobinger-Papamantellos et al. [8] are almost the same.

### Table 2. Magnetic space group in the family of the crystallographic \( I4/mcm \) space group [10]

<table>
<thead>
<tr>
<th>( I4/mcm )</th>
<th>( I4/m'cm )</th>
<th>( I4'/mcm' )</th>
<th>( I4'/mc'm' )</th>
<th>( I4'/mc'm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I4/mcm )</td>
<td>( I4/m'cm )</td>
<td>( I4'/mcm' )</td>
<td>( I4'/mc'm' )</td>
<td>( I4'/mc'm )</td>
</tr>
</tbody>
</table>

The magnetic space groups in column A can be ruled out immediately since they do not comprise \( I_p \). Furthermore, the Pr-1 atom at the Wyckoff position \( 8f \) has a point symmetry group 4. The magnetic space group cannot have a \( 4' \) component since the \( 4' \) symmetry is not an admissible magnetic point group. Thus, four of the eight possible magnetic space groups in column B can be skipped. However, none of the remaining magnetic space groups permits the magnetic moment to point along the \( a \) or \( b \) axis which gives rise to the \((0 \ 0 \ 1)\) reflections.

### Table 3. Refined atomic parameters of \( \text{Pr}_6\text{Fe}_5\text{Sn} \) at 150 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>Point symmetry</th>
<th>( \mu_B(\mu_B) )</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( \text{Ui/}U_e^*100 \text{ (nm}^2\text{)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-1</td>
<td>( 8f )</td>
<td>4</td>
<td>2.1(4)</td>
<td>0</td>
<td>0</td>
<td>0.1060(4)</td>
<td>0.99(3)</td>
</tr>
<tr>
<td>Pr-2</td>
<td>( 16l )</td>
<td>( m )</td>
<td>1.9(4)</td>
<td>0.1620(7)</td>
<td>0.6620(7)</td>
<td>0.1866(3)</td>
<td>1.40(2)</td>
</tr>
<tr>
<td>Fe-1</td>
<td>( 16l )</td>
<td>( m )</td>
<td>2.0(4)</td>
<td>0.1798(3)</td>
<td>0.6798(3)</td>
<td>0.0587(2)</td>
<td>0.72(3)</td>
</tr>
<tr>
<td>Fe-2</td>
<td>( 16l )</td>
<td>( m )</td>
<td>2.4(4)</td>
<td>0.3868(3)</td>
<td>0.8868(3)</td>
<td>0.0939(2)</td>
<td>0.69(5)</td>
</tr>
<tr>
<td>Fe-3</td>
<td>( 16k )</td>
<td>( m )</td>
<td>2.0(4)</td>
<td>0.0665(4)</td>
<td>0.2097(4)</td>
<td>0</td>
<td>0.64(2)</td>
</tr>
<tr>
<td>Fe-4</td>
<td>( 4d )</td>
<td>( mmm )</td>
<td>2.0(4)</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.27(3)</td>
</tr>
<tr>
<td>Sn</td>
<td>( 4a )</td>
<td>422</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>1.24(4)</td>
</tr>
</tbody>
</table>

### Table 4. Refined atomic parameters of \( \text{Pr}_6\text{Fe}_5\text{Sn} \) at 1.5 K [8]

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( \mu_B(\mu_B) )</th>
<th>( B(\text{nm}^2)\times10^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-1</td>
<td>( 8f )</td>
<td>0</td>
<td>0</td>
<td>0.1044(4)</td>
<td>2.91(8)</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>Pr-2</td>
<td>( 16l )</td>
<td>0.1644(5)</td>
<td>0.6644(5)</td>
<td>0.1866(2)</td>
<td>2.73(5)</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>Fe-1</td>
<td>( 4d )</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>2.3(2)</td>
<td>0.18(3)</td>
</tr>
<tr>
<td>Fe-2</td>
<td>( 16k )</td>
<td>0.0655(3)</td>
<td>0.2104(2)</td>
<td>0</td>
<td>2.57(7)</td>
<td>0.18(3)</td>
</tr>
<tr>
<td>Fe-3</td>
<td>( 16l )</td>
<td>0.1785(2)</td>
<td>0.6784(2)</td>
<td>0.0588(1)</td>
<td>2.42(7)</td>
<td>0.18(3)</td>
</tr>
<tr>
<td>Fe-4</td>
<td>( 16l )</td>
<td>0.3865(2)</td>
<td>0.8865(2)</td>
<td>0.0937(1)</td>
<td>2.54(7)</td>
<td>0.18(3)</td>
</tr>
<tr>
<td>Sn</td>
<td>( 4a )</td>
<td>0</td>
<td>0.25</td>
<td>0.25</td>
<td>0.09(4)</td>
<td>0.09(4)</td>
</tr>
</tbody>
</table>
Fig. 1. The observed (dots), calculated (solid lines) and difference x-ray diffraction pattern of the Pr$_6$Fe$_{13}$Sn sample.

CONCLUSIONS

The Neutron diffraction work on the Pr$_6$Fe$_{13}$Sn has shown that the compound was antiferromagnetically ordered. The magnetic structure of Pr$_6$Fe$_{13}$Sn could be described as ferromagnetic blocks of parallel moments of Pr and Fe sublattices embedded between two successive Sn layers perpendicular to z located at z=0.25, 0.25 and 0.75. The moments of these blocks changed their sign collectively when moved to the adjacent block along the c-axis. The refined Pr moments at 150K were (2.1±0.4) and (1.9±0.4) $\mu_B$ for the 8f and 16l sites whereas the average of the Fe moments was (2.0±0.4) $\mu_B$.

ACKNOWLEDGEMENTS

Suharyana would like to thank the AUSaid for the scholarship. This work partly was founded by the Australian Research Grant.

REFERENCES


