Neutron Diffraction Study on the Magnetic Structure of $Pr_6Fe_{13}Sn$

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ABSTRACT

We have successfully prepared a $Pr_6Fe_{13}Sn$ 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 $Nd_6Fe_{13}Si$ 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 I_p 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) μ_B whereas the Pr moments are (2.1±0.4) and (1.9±0.4) μ_B for the 8*f* and 16*l* sites, respectively

INTRODUCTION

Compounds with a chemical formula $R_6Fe_{13}X$ (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 $Nd_2Fe_{14}B$- or $Pr_2Fe_{14}B$- type permanent magnets. It is believed that the role of the second phase of $R_6Fe_{13}X$-type may enhance the coercivity in $Nd_2Fe_{14}B$-type permanent magnets with an X element addition. Since the $Nd_2Fe_{14}B$-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 $R_6Fe_{13-x}X_{1+x}$ was unrevealed in 1985 by Siechevich *et al*. [1]. Particularly they have shown that compound $La_6Co_{11}Ga_3$ orders in a tetragonal structure with space group *I4/mcm*. Later on, Allemand *et al*. [2] have shown that $Nd_6Fe_{13}Si$ crystallizes as an ordered variant of this compound. The crystal structure is rather complicated with four different Fe sites, namely 16*k*, 16*l*₁, 16*l*₂, and 4*d*, two Nd nonequivalent sites, 8*f* and 16*l*, and one Si site 4*a*, forming a naturally layered atomic arrangement. The R atoms, especially those at the 16*l* 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 $R_6Fe_{13}X$ has arisen. Claims about ferromagnetism [4], ferromagnetism with compensation point [5], and antiferromagnetism [6] have been made. This controversion has prompted us to prepare six $R_6Fe_{13}X$ 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, [57]Fe 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 [57]Co 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 Lake-Shore Closed-cycle suseptometer at 137 Hz. Nèel temperatures were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7, using the heat capacity peak at T_N to signal ordering. We have shown that the compounds order antiferromagnetically at room temperature [7].

It should be noted that neutron diffraction experiment on $Pr_6Fe_{13}Sn$ performed at temperature 1.5K was reported [8]. They reported the R atom at the 16*l* site is weakly magnetic and its refined magnetic moment at room temperature is almost zero. Here, we present our neutron diffraction study

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of $Pr_6Fe_{13}Sn$ compound in order to reexamine the paper of Schobinger-Papamentallos *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 $Pr_6Fe_{13}Sn$ 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 a SIEMENS D5000 diffractometer. Cu-Kα was used. The step increment in 2θ was 0.05° and the 2θ scanning speed was 0.5° per minute. The pattern was collected in the 2θ region 25° - 60°. Constant wavelength neutron diffraction experiment on the $Pr_6Fe_{13}Sn$ polycrystalline powder sample was performed at the Berlin Neutron Scattering Centre, Hahn-Meitner Institute in Berlin. The data were collected on the high resolution diffractometer of E9 (λ=1.58313Å) at temperature 150 K. The step increment in 2θ was 0.1° and the data were collected in the 2θ region 3 – 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 $Pr_6Fe_{13}Sn$ 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 $Nd_6Fe_{13}Sn$ 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_{wp} =1.97 and χ^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 $Pr_6Fe_{13}Sn$ structure types reported previously by Allemand *et al*. [2]. In other words, the sample is virtually single-phase. The final refined lattice constants of $Pr_6Fe_{13}Sn$ 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 $Pr_6Fe_{13}Sn$ deduced from x-ray diffraction data.

atom	site	x	y	z
Nd-1	8*f*	0	0	0.1072(8)
Nd-2	16*l*	0.1605(9)	0.6590(8)	0.1862(7)
Fe-1	16*l*$_1$	0.1725(8)	0.6815(7)	0.0575(7)
Fe-2	16*l*$_2$	0.3811(8)	0.8823(7)	0.0946(7)
Fe-3	16*k*	0.0621(9)	0.2042(8)	0
Fe-4	4*d*	0	0.5	0
Sn	4*a*	0	0	0.25

The magnetic structure of $Pr_6Fe_{13}Sn$ has been investigated using powder neutron diffraction by Schobinger-Papamantellos *et al*. [11]. The magnetic unit cell of $Pr_6Fe_{13}Sn$ 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 $Pr_6Fe_{13}Sn$ due to [11] was displayed.

Neutron diffraction pattern of the polycrystalline powder $Pr_6Fe_{13}Sn$ 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 2θ = 3.4°. Since the diffraction condition for the space group *I*4/*mcm* is $h + k + l = 2n$, the occurrence of the (0 0 1) peak indicates that the magnetic ordering of $Pr_6Fe_{13}Sn$ is antiferromagnetic. Furthermore, the magnetic lattice of $Pr_6Fe_{13}Sn$ is I_p 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 *I*4/*mcm* space group. They are presented in Table 2.

Table 2. Magnetic space group in the family of the crystallographic *I4/mcm* space group [10]

A	B
I4/mcm	I_p4/mcm
I4/m'cm	$I_p4/m'cm$
I4'/mc'm	$I_p4'/mc'm$
I4'/mcm'	I_p4'/mcm'
I4'/m'c'm	$I_p4'/m'c'm$
I4/mc'm'	$I_p4/mc'm'$
I4'/m'cm'	$I_p4'/m'cm'$
I4/m'c'm'	$I_p4/m'c'm'$

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 8*f* 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 *l*) reflections.

The neutron patterns of the $Pr_6Fe_{13}Sn$ collected at 150 K was analyzed by employing the magnetic structure model of $Pr_6Fe_{13}Sn$ proposed by Schobinger-Papamantellos *et al*. [11]. Fig. 3 shows the neutron diffraction pattern of the $Pr_6Fe_{13}Sn$ recorded at 150 K. The reliability factors are R_{wp}=9.5 % and R_p=7.1 % and χ^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) μ_B at 150 K. The respective magnetic moment values of Pr 8*f* and 16*l* sites are 2.1 (4) and 1.9 (4) μ_B. These values are below the magnetic moment of free Pr^{3+} ion value $gJ = 3.2\mu_B$. The refined crystal constants of $Pr_6Fe_{13}Sn$ 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 3. Refined atomic parameters of $Pr_6Fe_{13}Sn$ at 150 K.

Atom	site	Point symmetry	$\mu_{xy}(\mu_B)$	x	y	z	Ui/Ue*100 (nm²)
Pr-1	8*f*	4	2.1(4)	0	0	0.1060(4)	0.99(3)
Pr-2	16*l*	*m*	1.9(4)	0.1620(7)	0.6620(7)	0.1866(3)	1.40(2)
Fe-1	16*l*₁	*m*	2.0(4)	0.1798(3)	0.6798(3)	0.0587(2)	0.72(3)
Fe-2	16*l*₂	*m*	2.4(4)	0.3868(3)	0.8868(3)	0.0939(2)	0.69(5)
Fe-3	16*k*	*m*	2.0(4)	0.0665(4)	0.2097(4)	0	0.64(2)
Fe-4	4*d*	*mmm*	2.0(4)	0	0.5	0	0.27(3)
Sn	4*a*	422		0	0	0.25	1.24(4)

Table 4. Refined atomic parameters of $Pr_6Fe_{13}Sn$ at 1.5 K [8]

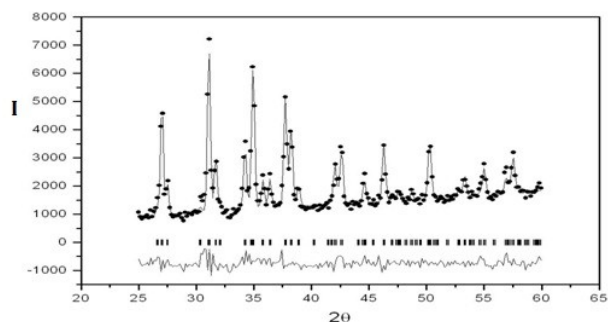| atom	site	x	y	z	$\mu_{xy}(\mu_B)$	B(nm²)x10²
Pr-1	8*f*	0	0	0.1044(4)	2.91(8)	1.0(1)
Pr-2	16*l*	0.1644(5)	0.6644(5)	0.1866(2)	2.73(5)	1.0(1)
Fe-1	4*d*	0	0.5	0	2.3(2)	0.18(3)
Fe-2	16*k*	0.0655(3)	0.2104(2)	0	2.57(7)	0.18(3)
Fe-3	16*l*₁	0.1785(2)	0.6784(2)	0.0588(1)	2.42(7)	0.18(3)
Fe-4	16*l*₂	0.3865(2)	0.8865(2)	0.0937(1)	2.54(7)	0.18(3)
Sn	4*a*	0	0	0.25		0.09(4)

Fig. 1. The observed (dots), calculated (solid lines) and difference x-ray diffraction pattern of the $Pr_6Fe_{13}Sn$ sample.
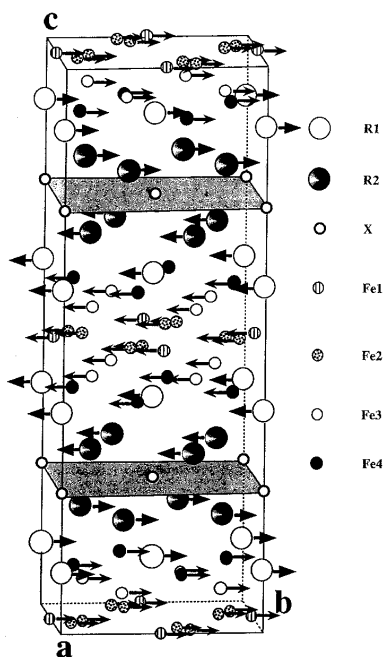

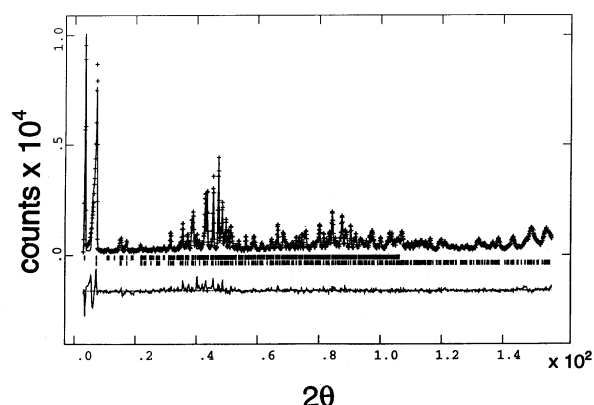**Fig. 2**. Schematic representation of the antiferromagnetic structure of $Pr_6Fe_{13}Sn$ [11]. In this work R = Pr, and X=Sn.

Fig. 3. Observed (crosses) and calculated (lines) neutron diffraction pattern of the $Pr_6Fe_{13}Sn$ recorded 150 K.

CONCLUSIONS

The Neutron diffraction work on the $Pr_6Fe_{13}Sn$ has shown that the compound was antiferromagnetically ordered. The magnetic structure of $Pr_6Fe_{13}Sn$ 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) μ_B for the 8f and 16l sites whereas the average of the Fe moments was (2.0±0.4) μ_B.

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