Structure and magnetocaloric effect of $Pr_2Fe_{17-x}Al_x$

L. Bessais[1], R. Guetari[1,2], R. Bez[1,2], K. Zehani[1], N. Mliki[2] and C. B. Cizmas[3]

[1]CMTR, ICMPE, UMR7182, CNRS-UPEC, 2 rue Henri Dunant F-94320 Thiais, France
[2]LMOP, Faculté des Sciences de Tunis, Université Tunis ElManar, 2092 Tunis, Tunisia
[3]Dep. of Electrical Engineering and Applied Physics, Transilvania University of Brasov, 500036 Brasov, Romania

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Abstract

In this work, we present the results of the substitution of aluminum for iron in Pr_2Fe_{17}. The polycrystalline $Pr_2Fe_{17-x}Al_x$ samples (x = 0, 0.25, 0.5, 0.75 and 1) were prepared by arc melting under a high purity argon and homogenized at 1373 K for one week to minimize the amount of other possible impurity phases. The samples were characterized using powder X ray diffraction (XRD) and were refined using Rietveld method with Fullprof program. The lattice parameters increases with the Al content (from a = 8.5646 Å and c = 12.4394 Å, for x = 0, to a = 8.6194 Å and c = 12.5163 Å, for x = 1) and all the samples crystallize in the $R\bar{3}m$ of the Th_2Zn_{17}. We can explain this increasing by the largest covalent radius of Al compared to Fe. In addition, we have shown that the Al substitution of Fe increases Tc from 285 K (for x = 0) to 361 K (for x = 1) due mainly to the magnetovolumic effect. The magnetocaloric effect (MCE) of these compounds has been investigated by measuring their magnetic properties. The magnetic entropy variation decreases slightly from 5.51 $Jkg^{-1}K^{-1}$ to 4.71 $Jkg^{-1}K^{-1}$ under a magnetic field change of 0 - 5T.

Introduction

Intermetallic compounds of the type of R_2Fe_{17} (R: rare earth) are considered as very attractive systems because of their interesting magnetic properties useful in permanent magnets or magnetic recording applications [1, 2, 3]. Due to the large magnetic moment of Fe atoms and their compare low Curie temperature (T_C), they have drawn attention as promising materials for room temperature magnetic refrigeration technology. In the last decade, magnetocaloric materials have received considerable attention. The current interest has been on magnetic refrigeration near room temperature which is energetically more favorable [4]. The MCE is an intrinsic property of magnetic materials described for the first time by Warburg [5]. The Praseodymium-based 2:17 compounds crystallize in the rhombohedral $R\bar{3}m$ space group Th_2Zn_{17} type structure. The Fe atoms occupy four inequivalent crystallographic sites ($6c, 9d, 18f$ and $18h$ in the Wyckoff site notation) and a unique $6c$ site is occupied by Pr [6]. Pr_2Fe_{17} compound have some advantages, such as a maximum of ΔS_M around room temperature. In this work, we present the structural results and magnetic properties of $Pr_2Fe_{17-x}Al_x$ alloys.

Experiment

The alloys with starting composition Pr_2Fe_{17} were prepared by co-melting the high purity elements in an induction furnace under an atmosphere of high purity Ar. The raw materials were used in the form of ingots with purities of 99.9% for Pr and for Fe. The polycrystalline $Pr_2Fe_{17-x}Al_x$ samples (x=0, 0.25, 0.5, 0.75 and 1) were prepared by arc melting. All ingots were wrapped on tantalum foil, homogenized in the high-purity argon atmosphere at 1373 K for one week to minimize the amount of other possible impurity phases followed by quenching in water. The crystal structure was studied by means of a Brucker X-ray diffraction (XRD) and was determined using Rietveld method [7]. We have completed this structural characterization by magnetic and magnetocaloric study in order to follow the effect of Al substitution for Fe on Curie temperature and magnetic entropy change. It was measured using Physical Properties Measurement System PPMS9T Quantum Design equipment. The $M(H)$ curves were plotted at T= 10 K and around 295 K with a maximum applied field of 90 kOe on sample in epoxy resin. Curie temperatures were determined from the $M(T)$ curves.

Results and discussion

Structure analysis

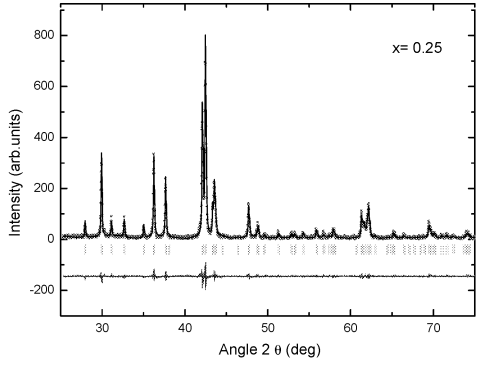

Figure 1: Rietveld analysis for $Pr_2Fe_{16.75}Al_{0.25}$ ingot.

Figure.1 shows, as an example, the XRD diagram of the of $Pr_2Fe_{16.75}Al_{0.25}$ ingot. The Rietveld refinement performed for the alloys show that the compound is single phase with the rhombohedral Th_2Zn_{17}-type structure (space group: $R\bar{3}m$) with unit cell parameters, a= 8.5760 Åand c= 12.4518 Å. The lattice parameters, the atomic positions, R_B and χ^2 factors, obtained from the best refinement are given in table 1 for the different aluminum content values (x) of $Pr_2Fe_{17-x}Al_x$. At small Al content 0 $\leq$x$\leq$ 1 , most of Al atoms

occupy the 6c site which has the largest Wigner-Seitz cell volume and the largest average site bond length.

It can be seen also that cell parameters for $Pr_2Fe_{17-x}Al_x$ increase with Al content while c/a is almost constant. The partial substitution of iron by aluminum resulted in a variation of the lattice parameters of our compounds and therefore, an increase of cell volume. The atomic radius of aluminum being greater than iron one, we would expect this evolution of crystallographic parameters.

Table 1: Structural properties of nanocrystalline $Pr_{2-x}Dy_xFe_{17}$ for (x = 0, 0.125,0.25, 0.375 and 0.5)

x	a(Å)	c(Å)	c/a	V(Å^3)	χ^2	R_B
0	8.5646(3)	12.4394(1)	1.452	790	1.59	3.08
0.25	8.5760(2)	12.4518(6)	1.452	793	1.38	4.5
0.5	8.5867(6)	12.4657(14)	1.452	795	1.14	4.676
0.75	8.6078(4)	12.4960(8)	1.452	802	2.92	10.79
1	8.6194(6)	12.5163(10)	1.452	805	1.91	8.33

Magnetic properties and magnetocaloric effect

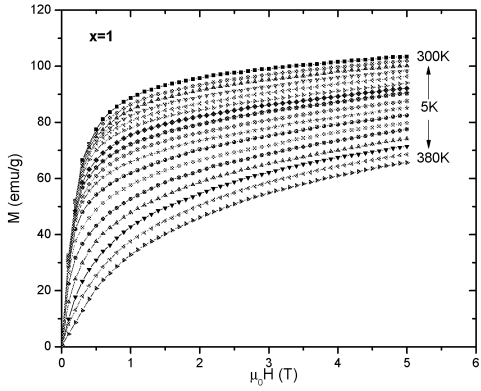

Figure 2: Isothermal magnetization of $Pr_2Fe_{16}Al_1$ in a field up to 5T in different temperature.

The value of T_C has been estimated from the minimum of the temperature derivative of the magnetization, dM/dT, vs. temperature [8]. We have shown that T_C increases

from 285 K, for x=0, to 361 K, for x=1. The relative increase of Curie temperature $\Delta T_C/T_C$ is around 27 % per Al atom. The magnetization isotherms $M(H)$ measured at different temperatures, ranging between 255 and 310 K with a step of 5 K, are presented in figure 2 for Pr_2 $Fe_{16.5}Al_{0.5}$ alloy.

The magnetization vs. applied magnetic field, $M(H)$ curves, shows a similar trend for the compounds. The saturation magnetization, M_S, has been estimated at 10 K from the fit of the $M(H)$ in the high applied magnetic field range (2-5 T) using a common approach to saturation law $M = M_S + a/H^2$. It can be seen that the saturation magnetization increases upon Al substitution reaching a maximum for x=0.5, then decreases.

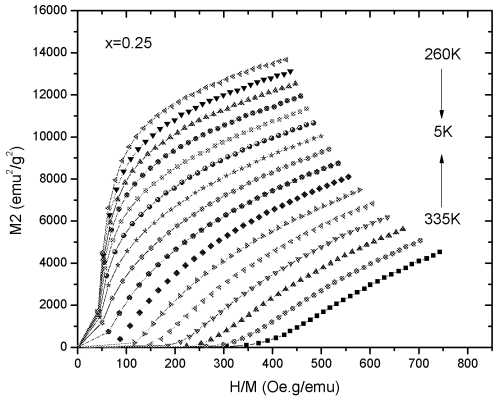

Figure 3: The Arrott plots of $Pr_2Fe_{16.75}Al_{0.25}$.

Figure 3 shows the Arrott plots of $Pr_2Fe_{16.75}Al_{0.25}$. It confirms the second-order magnetic transition in these compounds. Negative slop or S-shaped Arrott plots near T_C means that the phase transition take place in first order. However, positive slop and linear behavior near T_C means that the magnetic phase transition is of second-order. No first order phase transition was observed in the R_2Fe_{17}.

Magnetic entropy change, ΔS_M was determined as a function of temperature T and the applied magnetic field H through the numerical integration of the isothermally measured $M(H)$ curves [9]. In fact, in order to calculate ΔS_M at a given temperature, a numerical integration of two consecutive $M_T(H)$ isotherms around such temperature and the numerical derivative with temperature is performed. The results from these calculations allow us to obtain the evolution of ?SM with temperature and/or applied field.

Figure4 illustrates the magnetic entropy change, ΔS_M , deduced from $M(H)$ of $Pr_2Fe_{16.5}Al_{0.5}$ as a function of temperature and the external field change.

A summary of magnetic characterization of the intermetallic $Pr_2Fe_{17-x}Al_x$ is given

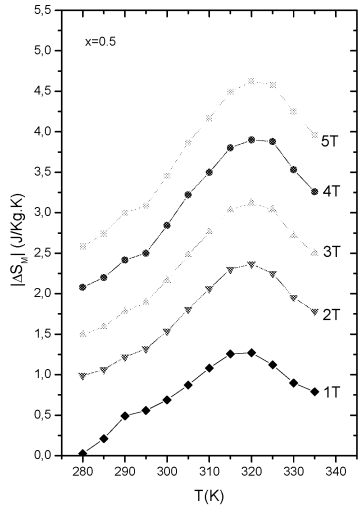

Figure 4: Magnetic entropy change ΔS_M vs temperature around the Curie temperature for $Pr_2Fe_{16.5}Al_{0.5}$

in table 2. One can see that the magnetic entropy change decreases from 5.51 $Jkg^{-1}K^{-1}$ (x=0) to 4.71 $Jkg^{-1}K^{-1}$ (x=1) under a magnetic field change of 0 - 5T. The saturation magnetization M_S increases upon Al substitution reaching a maximum for x=0.5, then decreases for x=0.75 and x=1.

Table 2: Results of the magnetic characterization of the $Pr_2Fe_{17-x}Al_x$: Curie temperature, magnetocristalline anisotropy, saturation magnetization M_s at 10 K and corresponding values of mean magnetic moment per formula unit.

x	0	0.25	0.5	0.75	1
T_C (K)	285	299	314	340	361
M_s ($emu.g^{-1}$)	165	168	170	163	161
M_s (μ_B/fu)	36.3	36.8	37	36.1	34.6
ΔS_M ($Jkg^{-1}K^{-1}$)	5.5	4.9	4.9	4.2	4.2

Conclusion

The structural and magnetic properties of $Pr_2Fe_{17-x}Al_x$ intermetallic compounds were performed. The influence of the Al substitution for Fe on the magnetic behavior of the Pr_2Fe_{17} compounds with $0 \leq x \leq 1$ was investigated. A single rhombohedral Th_2Zn_{17} phase was obtained after one week heat treatment at 1373 K for arc melting samples. The crystal structure of the parent Pr_2Fe_{17} was found to remain conserved for $Pr_2Fe_{17-x}Al_x$ compounds and crystallized in rhombohedral with a space group $R\bar{3}m$. The unit-cell volume V increases linearly at a rate of about 15 $Å^3$ per Al atom. Upon aluminum substitution, a considerable increase of T_C was observed. The values of Curie temperature are between 285 and 361 K. The entropy change ΔS_M between 0 and 5 T was calculated.

Acknowledgments

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