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Effect of Fe substitution on structural and magnetic properties of $Pr_2Co_{7-x}Fe_x$ compounds

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Abstract. This work focuses on the synthesis, structure, and magnetic properties of Pr-Co-Fe compounds. Our previous study of Pr_2Co_7 alloys with high coercivity is shown that for samples annealed at T_a= 800 °C, the main phase is hexagonal of the Ce_2Ni_7 type structure. This leads to the formation of a magnetically hard Pr_2Co_7 phase; the coercivity being equal to 18 kOe at 293 K and 23 kOe at 10 K and important saturation magnetization. These performances are due to the combination of the complementary characteristics of 3d-itinerant and 4f-localized magnetism of Co and Pr, respectively. Its Curie temperature is about 600 K. The aim of this study is to follow the effect of partial substitution of Co by Fe on $Pr_2Co_{7-x}Fe_x$ structural and magnetic properties, where x = 0.25, 0.50, 0.75 and 1. These compounds were synthesized by mechanical alloying. The Rietveld analysis of DRX shows that these intermetallics, annealed at T_a = 700 °C, adopt mainly hexagonal Ce_2Ni_7 type structure with $P6_3/mmc$ group space. Moreover, it points out a lattice expansion along the c axis after Fe substitution for Co. Furthermore, these hexagonal phases possess magnetic properties more attractive than Pr_2Co_7, the Curie temperatures are higher than Pr_2Co_7 ones and the highest is obtained for x = 0.5 where T_C = 760 K. This increase is due to the well-known electronic effect that invokes the reduction of antiferromagnetic coupling. These phases are particularly promising for permanent magnet applications.

Introduction

In recent years, the rare-earth-transition metal intermetallic compounds have become well established as an important new class of permanent magnet materials [1, 2]. Among these compounds, the Pr_2Co_7 alloy is currently one of the most promising. It has a high Curie temperature, T_C = 600 K, and an uniaxial magnetocrystalline anisotropy. In addition, the study of extrinsic magnetic properties of the Pr_2Co_7 compound revealed the existence of a large coercive field of about 18 kOe at 293 K and 23 kOe at 10K, a high remanent magnetization and an important saturation magnetization M_S [3]. These performances are due to the combination of the complementary characteristics of 3d-itinerant and 4f-localized magnetism of Co and the rare earth (Pr, Sm,...),

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respecively [4]. The reason for the high T_C is due to the predominance of the interactions Co-Co [5, 6].
In this paper, we report crystal structure and magnetic properties of $Pr_2Co_{7-x}Fe_x$ compounds obtained when cobalt is substituted by iron in Pr_2Co_7. Substitution will change the local environment of neighboring atoms and therefore the exchange interaction they undergo.

1 Experiments

The $Pr_2Co_{7-x}Fe_x$ (x = 0.25, 0.5, 0.75, 1) alloys were prepared by high-energy ball milling. An excess of Praseodymium powder was used in order to maintain an overpressure of Pr on the sample. The samples were examined by means of X-ray powder diffraction (XRD) using a Brucker diffractmeter with Cu K_α radiation. The XRD data were used for structure refinement were collected in a step-scan mode with a sampling time of 22 s and a sampling step of 0.04° in the 2θ range of 25-80°. An internal Si standard (NBS, SRM 640) was used to measure the unit cell parameter with an accuracy of $\pm 1\times10^{-4}$A. The pattern refinement was performed with the FULLPROF computing code based on the Rietveld technique, in the assumption of Thompson-Cox-Hastings line profile [7, 8]. The goodness-of-fit indicators R_B and χ_2 are calculated as usual and described earlier [9]. The magnetization was measured using a differential sample magnetometer (MANICS). When necessary, the samples were sealed in silica tubes to avoid oxidation upon heating. Thermomagnetic data were measured under an applied field of 1000 Oe with a heating rate of 10 K/min. The Curie temperature T_C was determined from the M-T curves by extrapolating the linear part of the M-T curve and finding the temperature values of the intersection with the extended baseline [10, 11]. For magnetic hysteresis measurements at T = 293 K, we used a Physical Properties Measurement System (PPMS) Quantum Design equipment in fields up to 9 kOe.

2 Results and discussion

2.1 Structure analysis

The XRD patterns and the corresponding Rietveld analysis of the $Pr_2Co_{7-x}Fe_x$ compounds, annealed at T_a= 700 °C, were systematically done for x =0.25, 0.5, 0.75 and x =1. Figure 1 shows, as an example, the results obtained for x = 0.5. One can see that the $Pr_2Co_{6.5}Fe_{0.5}$ phase is present with 98.64% and adopts mainly a hexagonal Ce_2Ni_7-type structure with $P6_3/mmc$ group space. The amounts of oxide are 1.36% for Pr_2O_3.

It is likely that the Fe atoms preferentially reside on the 6h sites. In fact, the best agreement factor was obtained with iron located in 6h position (Table1). The Rietveld refinement, carried out with a single domain size of diffraction self-consistent with a diameter of 60Å, leads to a R_B factor equal to 1.2%. The atom positions and related data obtained by Rietveld refinement of the $Pr_2Co_{6.5}Fe_{0.5}$ alloy are reported in Table 2.

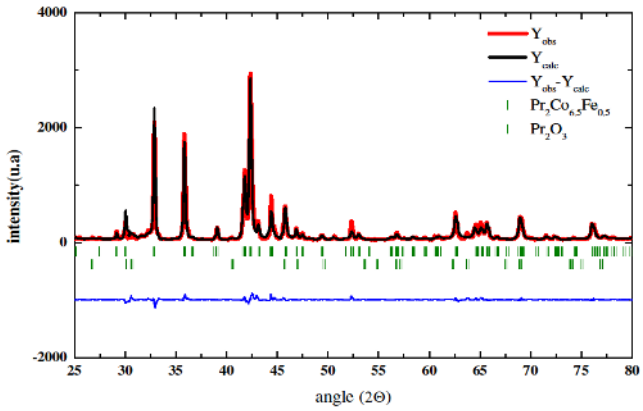

Fig. 1. Rietveld analysis for X-ray diffraction pattern of $Pr_2Co_{6.5}Fe_{0.5}$, annealed at 700 °C.

Table 1. The values of R_B factor and χ_2 from Rietveld refinement for the Fe occupancy in different crystallographic positions.

	12k	**6h**	**4f**	**4e**	**2a**
R_B	2.2	1.2	4.6	3.9	6.5
χ_2	3.7	3.2	4.5	5.3	7.8

Table 2. Rietveld refinement results for the atomic positions in a unit cell of the $Pr_2Co_{6.25}Fe_{0.5}$ compound.

Atom	**Position**	**x/a**	**y/b**	**z/c**
Co1	12k	0.1662	0.3324	0.0854
Co2+Fe	6h	0.1647	0.3296	1/4
Co3	4f	1/3	2/3	0.1666
Co4	4e	0	0	0.1670
Co5	2a	0	0	0

Table 3 shows the variations of parameters obtained in the solid solution $Pr_2Co_{7-x}Fe_x$ for all samples annealed at 700 °C. It appears that the a and c parameters increase slightly with increasing the Fe content. Then, we observe a unit cell volume expansion. Basically, because Fe has a larger atomic radius than Co, an expansion of lattice is expected with increasing substitution of Co by Fe. Moreover, the variation of c/a ratio with Fe content suggests that the unit cell expansion is anisotropic and more pronounced in the basal plane.

Table 3. a and c cell parameters, grain size Φ from Rietveld fit for $Pr_2Co_{7-x}Fe_x$ compounds.

	0.00	**0.25**	**0.50**	**0.75**	**1.00**
a(Å)	5.068(2)	5.068(3)	5.076(1)	5.079(2)	5.101(3)
c(Å)	24.457(3)	24.461(5)	24.473(7)	24.465(2)	24.415(5)
c/a	4.825	4.826	4.821	4.816	4.786
V(Å^3)	544.01	544.09	546.08	546.55	550.17
Φ(nm)	6	7	6	7	8

2.2 Intrinsic magnetic properties:

Thermomagnetic analysis indicates that $Pr_2Co_{7-x}Fe_x$ compounds are ferromagnetic with Curie temperature increasing significantly upon iron substitution. The magnetization curves M-H of Pr_2Co_7 and $Pr_2Co_{6.5}Fe_{0.5}$ samples are presented in Figure 3. The temperature dependence of the magnetization for Pr_2Co_7 and $Pr_2Co_{6.5}Fe_{0.5}$ samples has a unique magnetic phase transition at the Curie temperature. The T_C of these compounds increases from 600 K for Pr_2Co_7 to 760 K for $Pr_2Co_{6.5}Fe_{0.5}$, then decreases for x = 0.25 and x = 1 respectively equal to 695 K and 667 K. This decrease is due to the magnetic dilution indeed. Let's note that the Curie temperature is the result of competition between two effects, the magnetovolumic one related to the distances Co-Co [10] and the electronic effect related to the filling of the 3d band of iron [12]. Table 4 shows the lengths of 6f-6f dumbbells in the rate of substitution for $Pr_2Co_{7-x}Fe_x$ compound. It is found that the variation in lengths of dumbbells is very low. We can conclude that the magnetovolumic effect is negligible and the high Curie temperature variation could be attributed to the electronic effect of substituted iron in 6h site which dilutes the negative interactions.

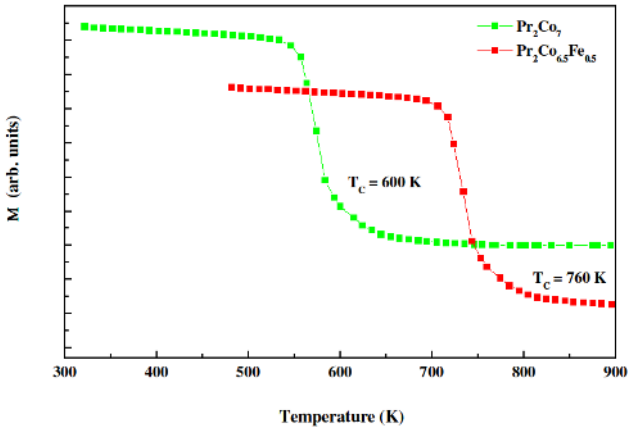

Fig. 2. The Curie temperature of Pr_2Co_7 and $Pr_2Co_{6.5}Fe_{0.5}$ compounds.

Table 4: Variation of Co(6h)-Co(6h) distances based vs Fe content

x	0.00	0.25	0.50	0.75	1
Co(6h)-Co(6h)	2.5091	2.5091	2.5092	2.5092	2.5093

The field dependence of magnetization of $Pr_2Co_{7-x}Fe_x$ compounds were measured at 293K in a magnetic field ranging from 0 to 90 kOe. All samples exhibit ferromagnetic character and tend to approach saturation in a field higher than 20 kOe. An example corresponding to x = 0.5 is shown in Figure 3. The saturation magnetization, M_S, is deduced using the saturation approach law $M(H)=M_S + a/H^2$ and converted to the magnetic moment per unit formula. The saturation moment μ_s of $Pr_2Co_{7-x}Fe_x$ increases from 8.32 to 12.28 μ_B/f.u with increasing Fe content from 0 to x = 1. Since the atomic moment of transition metal may be underestimated if the crystal-field effect of Pr moment is taken into account, the large atomic moment of the transition metal implies that the compound becomes strong ferromagnetic as the substitution of Fe for Co increases.

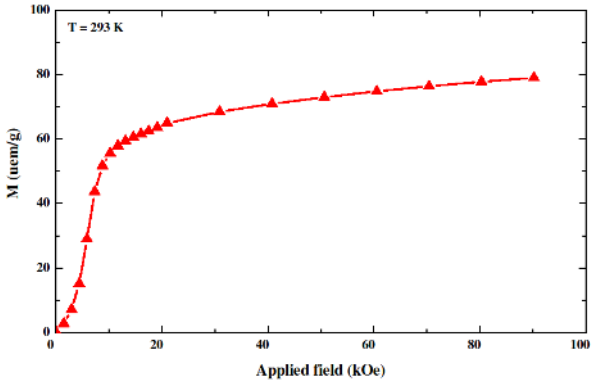

Fig. 3. Field dependence of the magnetic moment of $Pr_2Co_{6.5}Fe_{0.5}$ compounds measured at 293 K.

2.3 Extrinsic magnetic properties: coercivity

The search for the optimized nanocrystalline state could lead to good extrinsic characteristics. In order to reach the best one, annealing at different temperatures were performed on many samples. For each annealing temperature, a measure M(H) is performed.
The hysteresis loop of the sample $Pr_2Co_{6.5}Fe_{0.5}$ annealed at 800 °C measured at 293 K is illustrated in Figure 4.

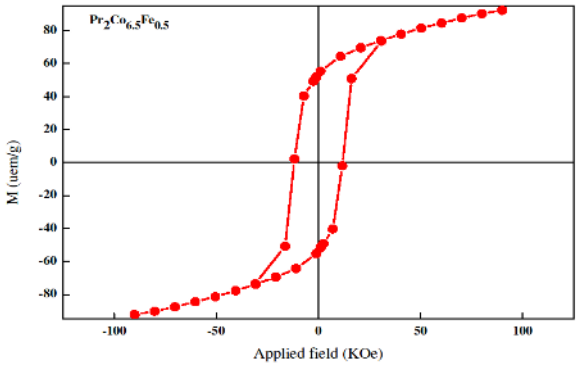

Fig. 4. Hysteresis loop of $Pr_2Co_{6.5}Fe_{0.5}$ annealing at 800 °C, measured at 293 K.

The microstructures revealing the best magnetic properties correspond to an annealing temperature ranging between 700 and 900 °C. The better coercivity measured at 293K is H_c = 13 kOe, Mr = 60 uem/g and M_r/M_{max} = 0.61 for x = 0.25 annealed at T_a = 700 °C, and H_c = 11 kOe , Mr = 57 uem/g and M_r/M_{max} = 0.68 for x = 0.5 annealed at T_a = 800 °C. The enhanced remanence ($M_r/M_{max} > 0.5$) suggests strong exchange interaction between the adjacent crystallites; characteristic of the nanocrystalline state, where the mean grain size is about 8 nm as determined by analysis Rietveld. These compounds are useful for applications in the field of permanent magnets, due to their high Curie temperature and high coercivity.

Conclusion

In conclusion, new $Pr_2Co_{7-x}Fe_x$ compounds with Ce_2Ni_7-type structure were synthesized. This solid solution is obtained by high energy milling followed by annealing for 30min. These compounds are ferromagnetic. The Curie temperature increases from 600 K to 760 K and the saturation magnetic

moment increases from 8.32 to 12.28 μ_B/f.u, when x varies between 0 and 1. In addition, the study of extrinsic magnetic properties of the $Pr_2Co_{6.5}Fe_{0.5}$ compound revealed the existence of a large coercive field about 11 kOe at 293K, and a high remanent magnetization of the order of 60 emu/g measured at room temperature for samples annealed at 800 °C. This leads to materials with magnetic properties in high-performance permanent magnets.

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