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Nanocrystalline Pr_2Fe_{17} studied by neutron powder diffraction

Pedro Gorria[1], Pablo Álvarez[1], Jorge Sánchez Marcos[2], José L Sánchez Llamazares[1] and Jesús A. Blanco[1]

[1] Departamento de Física, Universidad de Oviedo, Av. Calvo Sotelo, s/n, 33007 Oviedo, Spain.
[2] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

E-mail: pgorria@uniovi.es

Abstract. We have used neutron powder diffraction to make a comprehensive study of the crystal structure in Pr_2Fe_{17} nanocrystalline compounds. These nanostructured materials have been obtained by high-energy ball milling from an arc-melted bulk polycrystalline alloy. The Th_2Zn_{17}-type rhombohedral crystal structure of the starting bulk alloy is maintained after milling for 10 and 20 hours. The studied alloys are ferromagnetic below T_C = 286±1 K (bulk) and $T_C \approx$ 300±20 K (milled). These materials exhibit strong magneto-volume anomalies below T_C, such as a negative coefficient of thermal expansion ($\alpha_V \approx -30 \times 10^{-6}$ K^{-1}).

Mechanical processing by means of high-energy ball milling technique (HEBM) is commonly used to obtain a huge number of alloys far from the thermodynamic equilibrium [1]. In particular, different Fe-TM binary compounds, where TM is a transition metal, can be synthesized with distinct degrees of disorder, i.e. metastable FeCu solid solutions [2], nanocrystalline FeNi powders [3] or FeZr amorphous alloys [4], among others. Furthermore, drastic microstructural changes in a bulk alloy, such as nanostructure formation, can be induced using HEBM, giving rise to modifications of the physical-chemical properties respect to those exhibited by the starting bulk alloy [5,6]. We report here a neutron powder diffraction study of the induced changes in the microstructure and in the magneto-volume anomalies when a Pr_2Fe_{17} bulk intermetallic compound is milled for 10 and 20 hours.

Fe-rich R_2Fe_{17} alloys crystallize in the Th_2Zn_{17}-type rhombohedral crystal structure ($R\bar{3}m$) when R is one of the light rare earths, and exhibit ferromagnetic order with Curie temperatures, T_C, around room temperature in the case of Pr or Nd [7,8]. The are four inequivalent crystallographic Fe sites in Pr_2Fe_{17} [9] (in Wyckoff notation, 6c, 9d, 18f and 18h respectively) and the local environments of these Fe atoms determine the ferromagnetic character of these alloys, because the sign and the magnitude of the magnetic interactions depends on the number of Fe next neighbours and especially on the Fe-Fe interatomic distances [7,10]. In particular, the distance between 6c-6c Fe atoms (located along the c-axis), the so-called “dumbbell site”, is lower than the critical distance of 2.45 Å [11,12], which induces a negative local magnetic interaction and therefore, antiferromagnetic coupling is favoured. The rest of the iron magnetic moments are parallel due to Fe-Fe positive interactions, and the magnetic energy is stored around the shortest interatomic distances [Fe(6c)-Fe(6c)] where negative interactions exist. The observed magneto-volume effects below the ordering temperature such as the large and negative thermal expansion along the c-axis are direct effects of the compensation between magnetic and elastic energies. Moreover, ferromagnetic R_2Fe_{17} compounds have attracted interest for their moderate magneto-caloric effect around room temperature (being the magnetic entropy change for a magnetic field variation from 0 to 50 kOe $|\Delta S_M| \approx 6$ J kg^{-1} K^{-1} in the case of R = Pr or Nd) [13].

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In Figure 1 we show the room temperature neutron powder diffraction patterns collected on the D2B two-axis high-resolution diffractometer (ILL, Grenoble, France). The peaks observed in the patterns correspond to the Bragg reflections of the rhombohedral Pr_2Fe_{17} phase with a $R\bar{3}m$ crystal structure, thus indicating that the milling procedure does not give rise to any structural transformation and/or the appearance of new crystalline phases. However, a large decrease of the peak intensity together with a line-broadening of the Bragg reflections is clearly observed in both BM-10h and BM-20h milled samples. From the peak-profile analysis [15,16], we obtain a mean crystalline size of 20±2 nm (in good agreement with that estimated from transmission electron microscopy [14]), while the induced microstrain is almost vanishing in contrast with that reported for Fe-TM milled alloys [3,16]. The latter suggest the milling process mainly produces a progressive grain fracturing due to the brittleness of these compounds. Moreover, an increase of the background intensity due to the induced structural disorder at the grain boundaries is clearly observed. In Table I we present the values for some characteristic structural parameters estimated from the Rietveld analysis of the diffraction patterns shown in Figure 1. It is worth noting that only subtle changes are observed in the values of the unit cell parameters and in the atomic positions. Only those corresponding to the Fe1(6c) and Pr(6c) show a tendency to increase and decrease with the milling time, respectively.

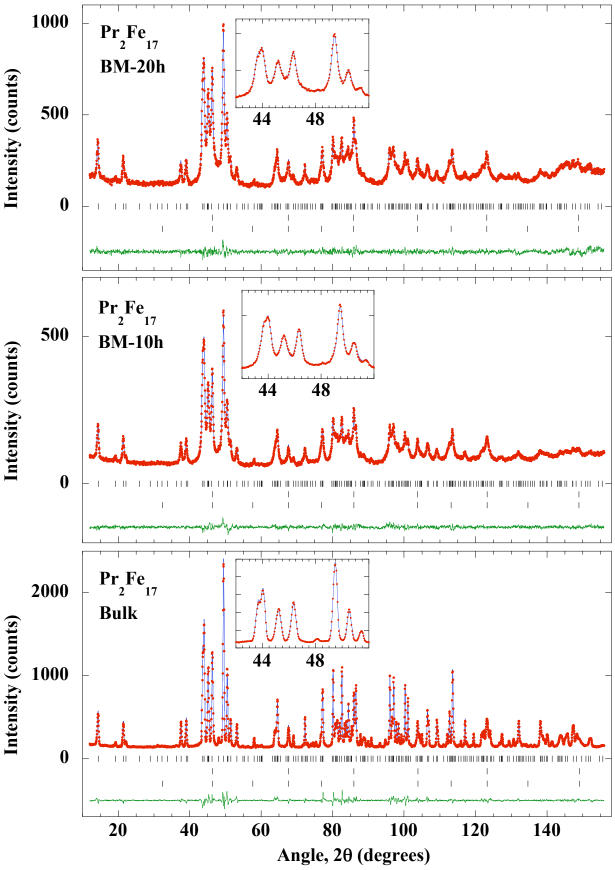

Figure 1. Observed (dots) and calculated (solid lines) neutron diffraction patterns. The position of the Bragg reflections is represented by vertical bars: first row corresponds to the Pr_2Fe_{17} phase while the second one is associated with α-Fe impurity. The observed-calculated difference is depicted at the bottom of each pattern. The insets show the peak broadening of the most intense reflections.

As previously mentioned, the magnetism of these compounds is strongly sensitive to the distance between Fe atoms at the "dumbbell sites", any increase of such Fe-Fe distance favors ferromagnetism [10-12]. Therefore, magneto-volume coupling acts as a driven force for the selective slight distortions induced by the milling process, thus affecting mainly to the 6c sites. In addition, it is observed a substantially increase in the value of the Debye-Waller temperature factor, B, for all the atomic positions in the milled samples. The significant increase of atoms at the grain surfaces and/or grain boundaries due to the drastic reduction in the average grain size during the milling procedure gives rise to structural disorder [16]; and can be the responsible for the higher values of B.

TABLE I. Structural data of Bulk and BM compounds at T = 300 K obtained from the neutron powder diffraction patterns shown in Fig. 1. Data for single crystal [9] is also reported for comparison

Compounds	Single crystal	Bulk	BM-10h	BM-20h
a (Å)	8.585(5)	8.5849(1)	8.5880(2)	8.5870(2)
c (Å)	12.464(8)	12.4659(1)	12.4699(2)	12.4679(3)
Pr(6c) z	0.3436(1)	0.3443(3)	0.3425(7)	0.3417(9)
Fe1(6c) z	0.0960(4)	0.0967(1)	0.0970(3)	0.0981(4)
Fe3(18f) x	0.2868(3)	0.2877(1)	0.2874(2)	0.2878(3)
Fe4(18h) x	0.1696(2)	0.1690(1)	0.1691(2)	0.1689(2)
y	0.8304(2)	0.8310(1)	0.8309(2)	0.8311(2)
z	0.4897(2)	0.4896(1)	0.4891(2)	0.4893(3)
B (Å^2) Pr(6c)	0.54(12)	0.65(6)	0.91(9)	1.01(12)
Fe1(6c)	0.55(15)	0.39(3)	1.43(7)	1.52(8)
Fe2(9d)	0.47(12)	0.29(2)	0.91(5)	0.98(7)
Fe3(18f)	0.66(12)	0.35(2)	1.09(4)	1.23(6)
Fe4(18h)	0.68(13)	0.35(2)	0.97(4)	1.02(6)
R_B(%)	3.9	3.3	2.5	2.4
χ^2		7.0	1.5	1.4

In order to check for the persistence of the magneto-volume anomalies after the strees-induced microstructural modification of the alloys, we have performed neutron powder thermo-diffraction experiments using the D1B two-axis diffractometer (ILL, Grenoble, France) in the temperature range between 5 and 300 K (see [4,16] for details). The temperature dependence of the cell volume for the three samples is depicted in figure 2.

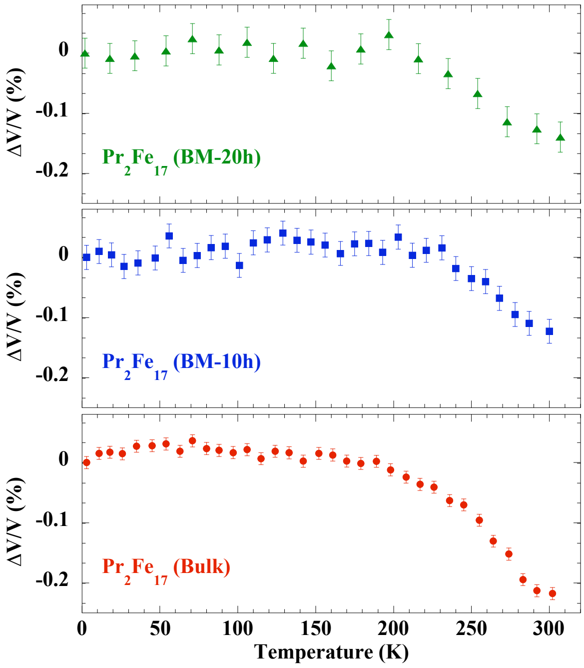

Figure 2. Temperature dependence of the unit cell volume, V, as deduced from neutron thermodiffraction experiments.

The three samples exhibit an almost constant value for the cell volume below 200 K, thus indicating a zero thermal expansion coefficient and the invar character in this temperature range. Taking into account that the Curie temperature of the Bulk alloy is $T_C \approx 286\pm1$ K [7,14], a minimum of the V(T) curve is expected around room temperature [10-12], as it can be observed in figure 2. For the milled samples this minimum is broader and shifted to higher temperatures, similar to that observed for the magnetization vs temperature curves, M(T) [13,14], where the decrease of M for T > 250 K is slower, making the estimation of an unique value for the Curie temperature ($T_C \approx 300\pm20$ K) extremely difficult in these disordered nanocrystalline alloys. Therefore, the temperature dependence of the $\Delta V/V$ is quite reminiscent of that associated with the magnetization M(T) [14]. This feature indicates the strong magneto-volume coupling in these materials, which is responsible for the moderate magneto-caloric effect found [13]. The slight increase of the estimated magnetic moments of the BM materials obtained from magnetization measurements is difficult to be observed from low temperature neutron diffraction patterns, owing to the significant line-broadening that mask the analysis.

In conclusion, high-energy ball milling allows obtaining nanocrystalline Pr_2Fe_{17} alloys with a mean crystalline size around 20 nm. The severe mechanical processing does not modify the crystal structure and the magneto-volume anomalies, including invar behaviour below 200 K and negative coefficient of thermal expansion around room temperature. The slight induced increase in the Fe-Fe interatomic distances at the “dumbbell” 6c sites causes the shift to higher temperatures for both the minimum of the temperature dependence of the cell volume as well as the T_C value. However, the decrease of the magnetization as well as that of the cell volume above 250 K is slower in the milled samples, probably due to the large amount of disorder generated at the grain boundaries. The latter suggests that a distribution of Curie temperatures must be considered as the most realistic picture for these disordered nanostructured materials, similarly to that occurring in other nanocrystalline systems [17,18].

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