MAGNETO-VOLUME ANOMALIES AND MAGNETOCALORIC EFFECT ON BALL-MILLING NANOSTRUCTURED Pr_2Fe_{17} COMPOUNDS

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Intermetallic Pr_2Fe_{17} alloy crystallizes in the rhombohedral Th_2Zn_{17}–type crystal structure (space group $R\bar{3}m$), showing a ferromagnetic behaviour with a high spontaneous magnetization below its Curie Temperature (T_C = 285 K) [1]. The interest on this compound has been recently renewed due to its relatively high magnetocaloric effect in a broad temperature interval around room temperature, and a relative cooling power even higher than the reported value for $Gd_5(Si_{1-x}Ge_x)_4$. Strong magneto-volumic anomalies are also present, such as anomalous thermal expansion. As the magnetic behaviour of this alloy is determined by exchange interactions between nearest-neighbours Fe atoms [2], changes in the structure can alter its magnetic properties. For this reason, we use high-energy ball milling in order to nanostructurate it with the aim of study the crystalline structure and the magnetic behaviour before and after milling. From the analysis of both X-Ray (K□ radiation Cu, □ = 1.5418 Å) and neutron at D2B (ILL) high resolution powder diffraction patterns, we conclude that after 10 hours milling (BM-10h) the almost single rombohedrical 2:17 phase persist with a slightly increase of cell parameters (less than 0.05%) and no evidence of microstrain due to the severe mechanical treatment, as it appears in other Fe-based compounds [3]. In addition, there is an important decrease of peak intensity and a huge broadening of the peak width after milling, which come from the formation of nanonoparticles with average crystalline grain size ≈ 20 nm. TEM images confirm that milled sample is nanostructurated with a grain size in the range 7 - 50 nm. An analysis of SEM images shows that these nanoparticles are forming micronic agglomerates with sizes of about 0.5 - 5.0 □m.

Magnetization as a function of temperature, measured under an applied magnetic field μ_0H = 20 mT, shows a well-defined T_C at 286 ± 1K in the case of bulk sample, whereas for the milled one is not possible to determine accurately a T_C, due to the fact that ferromagnetic to paramagnetic transition becomes broad. Moreover, this transition temperature shifts toward larger temperatures (305 ± 15 K). Magnetocaloric effect, i.e. the variation of magnetic entropy with magnetic field and temperature, is evaluated from the M(H,T) curves. A decrease of the peak of |□S_M| from 6.3 to 4.5 J kg^{-1} K^{-1} under an applied magnetic field μ_0H = 5 T for both bulk and ball milled samples respectively is observed. Nevertheless, a broadening on the |□S_M(T)| curve entails an increase of the RCP value, defined as the product of |□S_M| peak value and the full width at half maximum.

Temperature dependence of cell volume is obtained from neutron thermo-diffraction experiments at D1B (ILL) in the temperature range 10 - 450 K. In Both samples the volume has a minimum near T_C, which is deeper and sharper in the case of bulk sample. Cell volume at 300 K (where milling process takes place) and 6c-6c Fe-Fe interatomic distances are greater in the milled one, which favours ferromagnetism and therefore increase the Curie temperature in the BM-10h sample.

References:

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Figures:

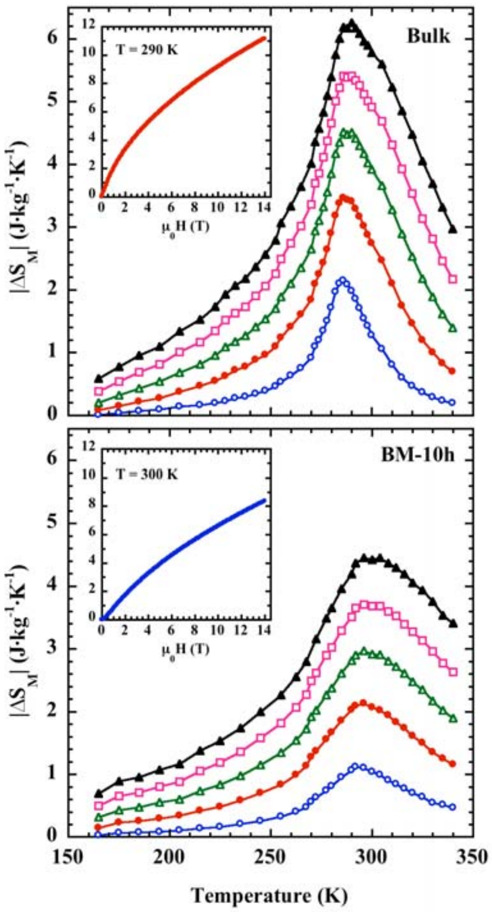

Fig. 1: Magnetic entropy change $|\Delta S_M|$ of Bulk (upper panel) and BM-10h (lower panel) samples under applied magnetic fields of 1 T (open circles), 2 T (solid circles), 3 T (open triangles), 4 T (open squares) and 5 T (solid triangles). The insets show $|\Delta S_M|$ vs. $\mu_0 H$ up to 14 T for each material