



Experimental realisation of off-stoichiometric Fe-Mn-Si full Heusler alloy with hexagonal crystal structure by pulsed laser deposition

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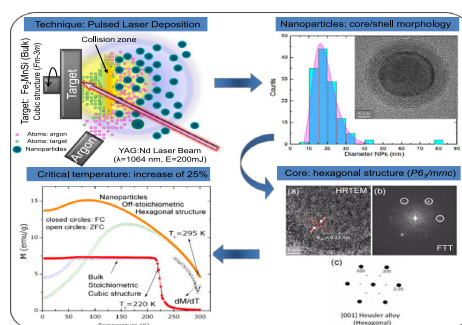
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HIGHLIGHTS

- Nanoparticles of Fe-Mn-Si full Heusler alloys, produced by pulsed laser deposition, present an hexagonal structure.
- Density functional calculations ratify the energy minima for this hexagonal structure.
- Due to the magneto-structural coupling on these materials, the Curie temperature increases 25%.
- These results open doors for new physical properties of Heusler alloys.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 September 2017

Received in revised form 29 January 2018

Accepted 30 January 2018

Available online xxxx

Keywords:

Nanoparticles

Pulsed laser deposition

Heusler alloys

Structural change

ABSTRACT

Full Heusler alloys are well known to either crystallize in a cubic structure (Cu_2MnAl -type), or present tetragonal distortions. Both structure types present interesting properties, like room temperature magnetic memory shape effect and/or remarkable magnetocaloric effect, mainly ruled by strong magnetostructural coupling. Due to this interplay, our aim was to produce a new crystal phase for the Heusler alloys, different from those well-established cubic and tetragonal, responsible for those well-known physical properties. Thus, we have produced nanoparticles of full Heusler alloys using a pulsed laser deposition technique (from targets of Fe_2MnSi) and obtained a core-shell pattern, presenting an amorphous shell and a crystalline core, with hexagonal symmetry. In accordance with these experimental findings, it was shown, by means of density functional calculation, the existence of a minimum of energy as a function of the hexagonal lattice parameters, with a true indication that the hexagonal phase is metastable. The magnetic properties differ considerably from those of bulk Fe_2MnSi , including an increase of the Curie temperature from 220 K to 295 K, which is of potential interest for room-temperature applications. This work opens the door to research in a new family of materials, whose properties have only now begun to be explored.

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1. Introduction

Heusler alloys are multifunctional materials, with extraordinary properties and a large amount of potential application in technological devices. Just to name a few, we can cite the magnetic

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transition close to room temperature, finely tuned to work in cooperation with the first order structural transition in the same temperature region [1]. This fact pushes this material to the top of the list of the most promising ones to be used as active magnetic regenerator in magnetocaloric devices [2]. We can also cite the shape-memory effect [3], in which some Heusler alloys undergo a mechanical transformation due to a thermal and/or magnetic field excitation. These kind of materials could replace pneumatic, electromagnetic and hydraulic drives in several devices; with the great advantage to be fast and precise under control by the magnetic field [4]. In spite of appearing to be independent phenomena, these examples are absolutely interconnected [5]; and this interplay of physical properties is the key role for the astonishing characteristics of the Heusler alloys. We can go beyond and cite some other important properties, such as: variable electronic structure, e.g., half-metallic ferromagnetism [6] and superconductivity [7]. Applications on solar cells [8] and topological insulators [9] are also discussed on the literature.

Heusler alloys are of the type X_2YZ (Cu_2MnAl -type structure - full Heusler) or XYZ ($MgAgAs$ type-structure - half Heusler), where X and Y are transition metals and Z belongs to either post-transition metals or metalloid groups [10]. Stoichiometric X_2YZ ternary compositions with $L2_1$ symmetry crystallize in Cu_2MnAl cubic structure with the space group $Fm\bar{3}m$, which is formed by four interpenetrating fcc sub-lattices. Two of these sub-lattices are occupied by X ions in the $8c$ ($1/4,1/4,1/4$) position, and the other two sub-lattices occupied by Y and Z ions in $4a$ ($0,0,0$) and $4b$ ($1/2,1/2,1/2$) positions, respectively. However, changes on this structure, still considering the stoichiometric composition, can be found due to atomic disorder, i.e., interchanges between the X , Y and/or Z ions. One of these changes leads to the $D0_3$ structure (X ions exchange position with Y ions); and it has consequences on the physical properties of the material, as already discussed by Vidal and co-workers [11], which pointed out that this change of structure has an impact on the anomalous Hall effect. However, considering the ternary compositions, the most relevant physical properties (mediated by the magneto-structural coupling above described and experimentally tuned to work in benefit of devices), are found on off-stoichiometric compositions; such as the magnetocaloric $Ni_{2.2}Mn_{0.8}Ga$ and $Ni_{2.1}Mn_{0.7}Ga$ compounds [1,12] and the magnetic-field induced strain and large magnetothermal conductive $Ni_{50}Mn_{50-x}In_x$ compositions [13].

On the other hand, structural changes can be found on the binary Mn_2MnZ ($Z = Ga$ and Ge), that can be packed in hexagonal, tetragonal or cubic phases (either bulk or thin films) [14–17]; and a special attention must be given to the case of Mn_3Ga , which assumes a hexagonal structure [14]. The transformation from the cubic phase to the hexagonal one was also observed in Fe_3Ge above 700 K [18]. These are examples of alloys, similar to the full Heusler 2:1:1, that present further transitions to other crystal structures, as the hexagonal one; however, these are binary.

Considering thus that the crystal structure plays an important role on the physical properties of these materials, our goal is to produce a ternary alloy with other symmetry, in order to uncover new physical effects and new magneto-structural correlations. We achieved this goal by producing core-shell nanoparticles (NPs) of Fe_2MnSi (nominal concentration) by means of Pulsed Laser Deposition (PLD) technique. We found a crystalline core with hexagonal structure and an off-stoichiometric composition of $Fe-Mn-Si$ Heusler alloy. From these achievements, the scientific community will be able to assess many open questions, like: the dependence of the physical properties of Heusler alloys with other (i) crystal packing and (ii) sample size; (iii) whether the high spin polarization or its half-metallic feature can be preserved in low dimension [19]; and many other issues.

2. Experimental and theoretical details

The polycrystalline target of Fe_2MnSi (nominal composition, $L2_1$ cubic structure) was obtained using conventional arc furnace technique, melted from a stoichiometric amount of iron, manganese (with an excess of 3% due to losses on melting [20]) and silicon. To ensure the homogenization of the 4 g target, it was sealed in a quartz tube, filled with Ar gas, annealed during 3 days at 1373 K and then quenched in water.

We have produced the NPs using a home-made Pulsed Laser Deposition (PLD), which is a technique for deposition of NPs in liquid media and in chambers with high gas pressures (~ 1 Torr). In the latter, plume expansion through the gas occurs, being a phenomenon much more complex than an expansion through the vacuum. The gas affects the plume dynamics and the spatial distribution and kinetic-energy distribution of atoms, ions and molecules, influencing NP nucleation and formation on-the-flight. These nanostructures formed by PLD are used for different applications such as solar cells [21,22], reflective coatings [23], photocatalysis [24,25], just to mention a few [26–28]. Our device uses a Nd:YAG laser with the following characteristic: wavelength of $\lambda = 1064$ nm; 7 ns of pulse duration; 10 Hz of repetition rate; and 200 mJ of energy per pulse. The substrate-target distance was 3 cm and, for deposition, the laser beam was focused on the target in the presence of an Ar buffer atmosphere of 1 Torr. A throughout description of the deposition procedure of this material was reported by some of us in reference [29]. These samples were prepared at IF-UFF.

Transmission Electron Microscopy (TEM) measurements were performed on a high resolution mode in a field emission JEOL 2100F, operated at 200 kV and equipped with a Noran 7 Energy Dispersive Spectroscopy detector. These measurements were made at CBPF-LABNANO. The magnetic properties were measured using a commercial Superconducting Quantum Interference Device (SQUID, from Quantum Design, model MPMS-XL), at IF-UNICAMP.

Complementary Density Functional Theory (DFT) calculations were performed to better understand the hexagonal phase experimentally found. These calculations were made using the PBE functional [30], as implemented in the Wien2K package [31], that uses the linearized augmented plane-wave + local orbitals (LAPW + lo) method. The RK_{max} parameter was set at 7.98, where RK_{max} is the product of the smallest atomic sphere by the largest K -vector in the plane wave expansion of the wave function. A total of 168 k -points in the Brillouin zone were considered. For these DFT calculations, the structure considered was a Mn_3Ga -like ($P6_3/mmc$ space group). Fe and Mn ions occupy the Mn site; while Si occupies the Ga site. To deal with the disorder, the Virtual Crystal Approximation was used [32]. One hexagonal unit cell comprised of 8 atoms was considered, together with periodic boundary conditions. These calculations were made at CICECO-UA.

3. Results and discussion

3.1. Transmission electron microscopy: morphology, crystallography and composition

To present our findings, let us start with a description of the morphology of the $Fe-Mn-Si$ NPs, followed by a comprehensive description of their crystal structure and magnetic behavior. Thus, to better understand the morphology of these NPs, we used transmission electron microscopy (TEM). To achieve this goal, these NPs were deposited directly on the surface of copper grids covered by a thin carbon film. The obtained particle size distribution (PSD) is presented on Fig. 1 - result obtained from several TEM images. It is worth to note the asymmetry of the distribution. For a better

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