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Experimental evidences of enhanced magnetocaloric properties at room temperature and half-metallicity on Fe_2MnSi-based Heusler alloys

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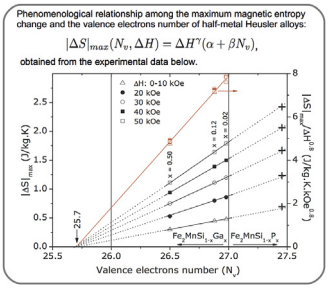
HIGHLIGHTS

- Multifunctional Heusler alloy: half-metallicity, enhanced magneto-caloric properties.
- Increasing of the entropy change DS by increasing the valence electrons number Nv
- Proposal of a phenomenological equation based on experimental data: DS (Nv)

GRAPHICAL ABSTRACT



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ABSTRACT

Heusler alloys are widely studied due to their interesting structural and magnetic properties, like magnetic shape memory ability, coupled magneto-structural phase transitions and half-metallicity; ruled, for many cases, by the valence electrons number (N_v). The present work focuses on the magnetocaloric potentials of half-metals, exploring the effect of N_v on the magnetic entropy change, preserving half-metallicity. The test bench is the Si-rich side of the half-metallic series $Fe_2MnSi_{1-x}Ga_x$. From the obtained experimental results it was possible to propose $|\Delta S|_{max} = \Delta H^{0.8}(\alpha + \beta N_v)$, i.e., the maximum magnetic entropy change depends in a linear fashion on N_v, weighted by a power law on the magnetic field change ΔH (α and β are constants experimentally determined). This phenomenological model opens doors for further theoretical investigations. In addition, it was also possible to predict a new multi-functional Heusler alloy, with enhanced magnetocaloric effect, Curie temperature close to 300 K and half-metallicity.

1. Introduction

Heusler alloys have been attracted considerable attention due to their several possible applications, such as on spintronics [1,2], magneto-optics [3], magnetoeletronics [4], solar thermoeletrics

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and other technological devices [5]. The physical properties for these applications, such as magnetization [2,6] and the Curie temperature [7,8], can be further optimized managing some parameters, as, for instance, lattice parameter and valence electrons numbers (N_v), in which are possible to be ruled by chemical substitution. An example of the above are alloys that were optimized to exhibit the curious shape memory behavior, defined as the ability of the material to come back to its original shape after deformed by a change in temperature and magnetic field; found, for instance, on Ni_{45} Co_5 $Mn_{36.6}$ $In_{13.4}$ [9]. Also remarkable is the magnetocaloric effect around the magnetic transition temperature due to the occurrence of coupled magneto-structural transitions; found, for instance, on non-stoichometric Ni–Mn–Ga alloys [10,11]. Other important example is the half-metallicity, in which the alloy presents a gap in the minority band, working therefore as a perfect spin filter, since electrons at the Fermi level are fully polarized. This feature is useful for spintronic purposes and is found, for instance, on Fe_2 MnSi [12], Fe_2 MnP [13] and the high temperature ferromagnets Co_2 MnSi and Co_2 MnGa [2]. The aim of this work is thus to predict a multifunctional Heusler alloy, with enhanced magnetocaloric effect at room temperature and half-metallicity.

More precisely, the magnetocaloric effect (MCE) has been studied by several researchers in order to develop magnetocaloric materials of low cost, good thermal conductivity, low electrical resistivity and mainly maximized magnetocaloric potential. The MCE can be seen from either an adiabatic or isothermal process, both due to a change of the applied magnetic field. From an adiabatic process, the magnetic material changes its temperature; while for an isothermal process it exchanges heat with a thermal reservoir. It is therefore possible to create a thermomagnetic cycle and a magnetic refrigerator based on these processes [14,15]. Some compounds that exhibit remarkable MCE potentials are, for instance, manganites [16–19]; MnAs-based compounds [20–23]; Heusler alloys [10,11]; La–Fe–Si alloys [24,25]; intermetallics like RNi_2 (R = Nd, Gd, Tb) [26], RCo_2 (R = Er, Tb) [27] and $PrNi_{1-x}$ Co_x [28]; and even diamagnetic materials like graphenes [29,30].

On the other hand, half-metal materials is one of the key rules to spintronics, since these materials are able to filter majority spins of an incoming non-polarized current. These are therefore useful for tunnel junctions, spin-injection and giant magnetoresistance devices [2], specially those with high Curie temperature. More precisely, the tunnel magnetoresistance ratio (TMR) become theoretically infinity based on the Julliere's model, for tunnel junctions using half-metals in both electrodes [31]. The half-metallicity can be verified from either the theoretical density of states, obtained from first-principle methods, or the total magnetic moment of the compound, that must obey the generalized Slater–Pauling rule $M = (N_v - 24)\mu_B$ [2], where N_v is the valence electrons number.

Considering this scenario, our aim is to provide a multifunctional Heusler alloy, with half-metallicity and enhanced magnetocaloric effect, tuning thus this multifunctionality with the valence electrons number N_v. To this purpose, our test bench materials are the Si-rich side of the half-metallic series Fe_2 $MnSi_{1-x}$ Ga_x, where N_v can be written as [12]:

$$N_v = (2 \times N_{Fe}) + N_{Mn} + (1 - x)N_{Si} + xN_{Ga} \quad (1)$$

Above, $N_{Fe} = 8$, $N_{Mn} = 7$, $N_{Si} = 4$ and $N_{Ga} = 3$ are the valence electrons for each atom.

2. Further details on the test bench material

The magnetic and structural properties of parent Fe_2 MnSi and Fe_2 MnGa Heusler alloys have been previously investigated [32–34]. The former is a well known half-metallic ferromagnet alloy with T_c around 224 K [12] and $Fm\bar{3}m$ spacial group (Cu_2 MnAl type structure); while Fe_2 MnGa is also a half-metallic ferromagnet with T_c far above room temperature, around 800 K as previously reported [34,35], and crystallizes in the $Pm\bar{3}m$ spacial group (Cu_3 Au type structure).

In spite of different crystallographic structures of those parent compounds, it is possible to achieve single phase samples of the series Fe_2 $MnSi_{1-x}$ Ga_x; however, only for the Si-rich side up to 50%, since the crystal structure of Fe_2 MnSi parent compound supports Ga substitution up to $x = 0.50$, with the lattice parameter a increasing by increasing Ga content [12]. In spite of these finds, the literature has no results on the magnetocaloric effect of these materials, but the Curie temperature of this series was detailed explored by this group and reported in reference [12]. This last was presented as a function of the valence electrons number N_v and an interesting linear behavior was found (see Fig. 1). Thus, since the aim of the present work is to provide a multifunctional Heusler alloy with enhanced magnetocaloric properties ruled by N_v and half-metallicity, from Fig. 1 it is straightforward to extrapolate the Curie temperature to 300 K and verify that $N_v = 27.44$ would bring the ferromagnetic transition up to room temperature (a desired feature expected to optimize magnetocaloric materials). Other studies connecting T_c and N_v confirm the linear growth tendency of these quantities for half-metallic Heusler alloys [5,36].

Thus, as a consequence of the above results, we must increase the valence electrons number N_v to further optimize the magnetocaloric properties of half-metal Heusler alloys. To achieve this goal, either Si or Ga must be replaced by other element (or elements) that can contribute with more electrons; i.e., those elements belonging to, for instance, group 15 of the periodic table, such as P or As. These elements contribute with 5 electrons and can indeed increase the overall valence electrons number of the system. On the other hand, a substitution by a group 14 element, such as Ge and Sn, does not increase the overall valence electrons number for this series, since these have only 4 valence electrons (the same valence electron number of Si). In fact, Zhang [37] found values for T_c between only 243 and 260 K in the same structural phase, by replacing Si by Ge in parental Fe_2 MnSi compound.

From the above, we propose therefore Fe_2 $MnSi_{0.56}$ $P_{0.44}$, since Kervan and Kervan [13] conducted an *ab initio* calculations concerning the Fe_2 MnP and confirmed the half-metallic features of the systems.

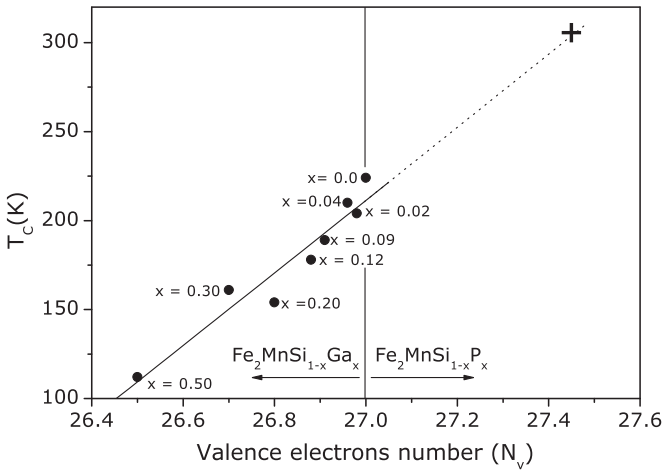

Fig. 1. Linear behavior of the Curie temperature (T_c) as a function of the valence electrons number N_v. The '+' signal marks the necessary N_v value to reach T_c at room temperature, found to be $N_v = 27.44$.