Distribution of Transition Temperatures in Magnetic Transformations: Sources, Effects and Procedures to Extract Information from Experimental Data

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Abstract: The presence of a distribution of transition temperatures (DTT) is ubiquitous in materials science. It is common to ascribe deviations from theoretical pure-phase behavior to this fact. To adapt the different pure phase models to systems with a DTT, the parameters of such distribution must be known or at least estimated. In this review, the different sources for the existence of such distributions and their effects on magnetothermal properties are summarized. In addition, different models proposed to extract the parameters of the corresponding DTT are discussed and extended, starting from Weiss model, to account for other phenomenologies. Experimental results on amorphous Fe-Nb-B and intermetallic MnCo(Fe)Ge systems are also reported.

Keywords: magnetic transitions; magnetostructural transitions; magnetoelastic transitions; distribution of transition temperatures

1. Introduction

Magnetic behavior of materials is diverse. Despite the existence of different magnetic orders, in this review, we focus on the transition between ferromagnetic (FM) and paramagnetic (PM) phases. For those systems where the coupling between magnetic and crystalline structure can be neglected, the transition from a low temperature ordered FM phase to a high temperature disordered PM phase is smooth. Magnetization at zero field drops to zero at a fixed temperature independently of the heating/cooling rate (i.e., the transition is not thermally activated). In fact, FM phase only applies in a certain temperature range and, if there is neither structural changes nor magnetoelastic coupling, a second-order phase transition (SOPT) takes place at the Curie temperature, $T_C$. Above this temperature, the exchange coupling is overcome by the thermal energy. To describe this magnetic transition, two limit models can be assumed [1]: long range, mean field (MF) approach (Weiss molecular field model), and short range, first neighbors approach (Heisenberg model).

Even in the case that the magnetic transition is not associated with a structural phase transition, coupling between magnetic and crystalline structures cannot always be neglected. In the case of magnetoelastically driven transitions, such as occurs for La(Fe, Si)$_{13}$ intermetallic [2], coupling between the cell volume and the molecular field constant of Weiss model yielded the development of Bean and Rodbell (BR) model [3]. This model successfully describes a continuous change from SOPT to first-order phase transition (FOPT) as the coupling parameter increases from a low temperature ordered FM to a disordered high temperature PM phase.

Magnetostructural transitions, such as those occurring in magnetic Heusler alloys [4], imply the reversible (although generally hysteretic) structural change from a low entropy, low symmetry, and low...
temperature phase (i.e., martensite) to a high entropy, high symmetry, and high temperature phase (i.e., austenite). Unlike the former described transitions, magnetostructural ones present a latent heat of the transformation and can be thermally activated (i.e., the transition temperature can be shifted with the heating or cooling rate) [5]. The magnetic nature of the austenite and martensite phases is diverse. It is possible to find both magnetostructural transformations: from a FM martensite to a PM austenite (implying an abrupt decrease to zero of the magnetization at the structural transition [6,7]) or from a PM martensite to a FM austenite (implying an abrupt increase from zero of the magnetization at the transition [8–10]). Moreover, transition from FM martensite to FM austenite can be also found [11], implying a step change in the magnetization. Transitions from PM martensite to PM austenite, although possible, are not of interest in our study frame as the zero-field magnetization is null for both structural phases.

Despite the careful preparation of the experimental samples, different factors (inhomogeneities, compositional gradients, crystal/particle size distributions, etc.) can lead to the appearance of non-single pure phase transitions. Deviations from the theoretical single-phase behavior can be corrected assuming a distribution of transition temperatures (DTT) in order to obtain a more realistic description of the behavior of the samples.

In Section 2, the main sources affecting Curie and magnetostructural transition temperatures are discussed. The presence of inhomogeneities in these sources (composition, crystal size, etc.), which can lead to the appearance of a DTT, is discussed.

Section 3 describes the effects produced by the existence of such DTT as well as some deviations from the theoretical predictions of single-phase models.

Section 4 describes different models used to extract the parameters of the DTT. Particularly, we extend one method recently proposed by the authors [12] to describe SOPT under mean field (MF) approach to account for the different types of transitions commented above. To describe systems out of MF frame, we use Curie transitions described by Arrott–Noakes (AN) equation of state (EOS) [13]. To describe magnetoelastic transitions, BR model is used. Finally, a simple model is developed to roughly describe magnetostructural transitions.

Section 5 presents some new experimental data to test the proposed model.

Finally, the main conclusions derived from this study are summarized.

2. Sources for a Distribution of Transition Temperatures

2.1. Compositional Dependence of Transition Temperatures

Compositional heterogeneity is the most intuitive source for the presence of a DTT through the compositional dependence of the transition temperatures (both Curie and magnetostructural ones). The close link between composition and temperature at which the transition occurs naturally yields a DTT when a certain gradient or heterogeneous compositional distribution exists. To estimate the importance of this source, as an example for SOPT, we can explore the dependence of Curie temperature $T_C$, in the frame of the Weiss model [1]:

$$T_C = \frac{g_J \mu_B (J + 1) M_S}{3 k_B} = \frac{n_V \lambda \mu_{\text{eff}}^2}{3 k_B}$$

where $g_J$ is the Landé factor; $\mu_B$ is the Bohr magneton; $J$ is the total angular momentum of the magnetic atom; $M_S$ is the saturation magnetization; $n_V$ is the number density of magnetic atoms; $\mu_{\text{eff}} = g_J \sqrt{(J + 1)} \mu_B$ is their effective magnetic moment; $k_B$ is the Boltzmann constant; and $\lambda$ is the molecular field constant (following Blundell’s book notation [1]). $\lambda$ has the same units as $\mu_0$, the permeability of vacuum). The $\lambda$ parameter is related to an effective exchange interaction, $J_{\text{ex}}$. Assuming a near neighbors approach:

$$\lambda = \frac{2zJ_{\text{ex}}(g_J - 1)^2}{n_V g_J^2 \mu_B^2}$$
where \( z \) is the number of near neighbors to which the atom is exchange coupled. In the case of transition metals ions, for which the orbital component of the angular moment is quenched, Equation (2) reduces to:

\[
\lambda = \frac{z J_{ex}}{2 \hbar \mu_B^2}
\]

(3)

The general case gives us a direct relation between \( T_C \) and the number of near neighbors, the exchange constant and the square of the effective magnetic moment:

\[
T_C = \frac{2 z J_{ex} \left( g_J - 1 \right)^2 \mu_{eff}^2}{3 k_B g_J^2 \mu_B^2} = \frac{2 z J_{ex} \left( g_J - 1 \right)^2 J (J + 1)}{3 k_B}
\]

(4)

where \( \left( g_J - 1 \right)^2 J (J + 1) \) is de Gennes factor. \( T_C \) of isostructural compositional series of rare earth (RE) compounds follows a linear trend with de Gennes factor [14,15].

Table 1 collects the experimental magnetic parameters for FM pure metals [1,16] and the effective \( J_{ex}/k_B \) from Weiss model. Despite this apparently clear picture, the presence of ferromagnetism is far from being easy to explain. In fact, calculated values of \( J_{ex} \) from direct exchange interaction are much lower than the experimental ones. The indirect exchange transmitted by the conduction electrons, as described by Ruderman, Kittel, Kasuya, and Yosida [1] (RKKY mechanism), can account for the magnetism in rare earths for which the magnetic moment is due to well localized \( f \) electrons and conduction electrons transmit the exchange [16]. However, the partially localized/itinerant nature of the \( d \) electrons responsible for the magnetic moment in transition metals adds complexity to the problem [17]. In any case, for metallic systems, the oscillatory dependence of \( J_{ex} \) with the atomic separation in metallic systems derived from RKKY interaction must be considered. In addition, magnetic moments of the atoms depend on composition (e.g., in binary systems [18]).

<table>
<thead>
<tr>
<th>Ferromagnet</th>
<th>( T_C ) (K)</th>
<th>Magnetic Moment (( \mu_B ))</th>
<th>Crystal Structure</th>
<th>( J_{ex}/k_B ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1043</td>
<td>2.22</td>
<td>bcc</td>
<td>159</td>
</tr>
<tr>
<td>Co</td>
<td>1394</td>
<td>1.715</td>
<td>hcp</td>
<td>237</td>
</tr>
<tr>
<td>Ni</td>
<td>631</td>
<td>0.605</td>
<td>fcc</td>
<td>862</td>
</tr>
<tr>
<td>Gd</td>
<td>293</td>
<td>7.98</td>
<td>hcp</td>
<td>2.3</td>
</tr>
<tr>
<td>Tb</td>
<td>220</td>
<td>9.77</td>
<td>hcp</td>
<td>2.6</td>
</tr>
<tr>
<td>Dy</td>
<td>89</td>
<td>10.83</td>
<td>hcp</td>
<td>1.5</td>
</tr>
<tr>
<td>Ho</td>
<td>20</td>
<td>11.24</td>
<td>hcp</td>
<td>0.5</td>
</tr>
<tr>
<td>Er</td>
<td>20</td>
<td>9.94</td>
<td>hcp</td>
<td>0.9</td>
</tr>
<tr>
<td>Tm</td>
<td>32</td>
<td>7.61</td>
<td>hcp</td>
<td>3.4</td>
</tr>
</tbody>
</table>

In the case of RE-based amorphous alloys, \( T_C \) increases as the amount of RE increases and it is maximum for Gd (see Figure 1a). For transition metal-based systems, as is found in Fe-based amorphous alloys, \( T_C \) is easily tunable by addition of non-magnetic or magnetic elements. When Co is partially substituted for Fe, a general increase of the Curie temperature is observed [19]. Despite the lower \( \mu_{eff} \) for Co or Ni than for Fe, a stronger \( J_{ex} \) is inferred for both Co and Ni pure systems. In the case of non-magnetic atom substitution (see Figure 1b), \( T_C \) decreases as Fe content increases in the alloy. Despite the larger number of magnetic moments, exchange is affected by the decrease in the distance between Fe atoms.
where \( \langle d \rangle \) deteriorates the double exchange mechanism and thus a decrease of \( T \) just a rude approximation. Generally, substitution of other transition element for Mn yields a deterioration of the double exchange mechanism and thus a decrease of \( T \) (Figure 2).

There is no clear correlation but a wide spread of \( T \) for three different families: RE\(_{55}\)Co\(_{20}\)Al\(_{25}\) [20,21], RE\(_{65}\)Fe\(_{20}\)Al\(_{15}\) [22,23], and RE\(_{70}\)Fe\(_{30}\) [24,25]. Other indirect exchange mechanism occurs in oxides. For example, double exchange in La\(_{1-x}\)Ca\(_x\)MnO\(_3\) is determined by the presence of two different valences in Mn ions [30]. However, the different ways to compositionally tailor this transition make this correlation just a rude approximation. Generally, substitution of other transition element for Mn yields a deterioration of the double exchange mechanism and thus a decrease of \( T \) [31].

\[
T = \frac{\langle R_{La} \rangle + R_O}{\sqrt{2}(\langle R_{Mn} \rangle + R_O)}
\]

where \( \langle R_{La} \rangle \), \( R_O \), and \( \langle R_{Mn} \rangle \) are the radii of the ions at lanthanum, oxygen, and manganese sites, respectively. However, the different ways to compositionally tailor this transition make this correlation just a rude approximation. Generally, substitution of other transition element for Mn yields a deterioration of the double exchange mechanism and thus a decrease of \( T \) [31].

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**Figure 1.** (a) \( T_C \) of rare earth (RE)-based amorphous alloys as a function of the average atomic number of the RE for three different families: RE\(_{55}\)Co\(_{20}\)Al\(_{25}\) [20,21], RE\(_{65}\)Fe\(_{20}\)Al\(_{15}\) [22,23], and RE\(_{70}\)Fe\(_{30}\) [24,25]. (b) \( T_C \) of Fe-B-Zr amorphous alloys as a function of the Fe content (data taken from [26–28] and supplemental material in [29]).

Other indirect exchange mechanism occurs in oxides. For example, double exchange in La\(_{1-x}\)Ca\(_x\)MnO\(_3\) is determined by the presence of two different valences in Mn ions [30]. However, there is no clear correlation but a wide spread of \( T_C \) data with respect to the fraction of Mn \(^{4+}\) ions (see Figure 2). \( T_C \) in these systems can be roughly, but better, correlated with the tolerance factor, \( t \), which relates the average ratios of the different ion sites as [31]:

\[
T = \frac{\langle R_{La} \rangle + R_O}{\sqrt{2}(\langle R_{Mn} \rangle + R_O)}
\]

where \( \langle R_{La} \rangle \), \( R_O \), and \( \langle R_{Mn} \rangle \) are the radii of the ions at lanthanum, oxygen, and manganese sites, respectively. However, the different ways to compositionally tailor this transition make this correlation just a rude approximation. Generally, substitution of other transition element for Mn yields a deterioration of the double exchange mechanism and thus a decrease of \( T \) [31].

**Figure 2.** \( T_C \) transition temperature as a function of the Mn \(^{4+}\) fraction in La-manganites (data taken from supplemental material of [29] and [31–37]).
Magnetoelastic transition occurring for La(Fe,Si)\textsubscript{13} phase is strongly dependent on the Si content \cite{2,38,39}. Despite the order character of the transition (FOPT for low Si content and SOPT for high Si content \cite{38}), an almost linear correlation is followed with this parameter (see Figure 3). The slope of this linear fitting yields a value of \(~4\) K change per at \% of Si. In this family of alloys, further tailoring of the transition is obtained by substitution of other elements such Co for Fe (increasing \(T_C\) \cite{40}) or other RE for La (decreasing \(T_C\) \cite{41}) or by addition of interstitial atoms, mainly H \cite{41} (increasing of \(T_C\)).

![Figure 3](image)

**Figure 3.** \(T_C\) transition temperature as a function of the Si content in La(Fe,Si)\textsubscript{13} system (data taken from supplemental material in \cite{29} and references therein).

In the case of magnetostructural transitions of Heusler alloys, the transition temperature, \(T_t\), from martensite to austenite phase is much more sensitive to the composition than the \(T_C\) of the high and low temperature phases. Figure 4 shows different transition temperatures as a function of the number of electrons per atom in the outer shells for the different families of Heusler alloys. It is observed that the slope of change in martensitic transformation is several times larger than the change in the Curie temperature of the austenitic phase, \(T^A_C\). In fact, as an example, whereas \(T^A_C\) is almost unaffected when composition changes from Ni\textsubscript{49.7}Mn\textsubscript{36.2}In\textsubscript{14.1} to Ni\textsubscript{49.8}Mn\textsubscript{35.0}In\textsubscript{15.2}, magnetostructural transition decreases \(~100\) K. This strong dependence in Mn/In ratio is even enhanced in Ni(Co)MnIn, for which 1 at.\% increase in Mn and decrease in In yields an increase in martensitic transformation of \(~150\) K \cite{9}.

![Figure 4](image)

**Figure 4.** Martensitic (solid symbols) and Curie (hollow symbols) temperatures as a function of the number of the outer electrons per atom for: (a) two families of half-Heusler alloys; and (b) four families of Heusler alloys (data taken from supplemental material in \cite{29} and references therein).
2.2. Other Factors Affecting Transition Temperature

Crystal size may influence the magnetic transition, particularly when this characteristic structural length (crystal size) becomes of the order of the magnetic exchange correlation length. This magnitude is related to the domain wall thickness, \( \delta \approx \sqrt{2A/K} \), where \( A \) is the exchange stiffness and \( K \) is the magnetic anisotropy constant. This occurs in the nanometer scale (e.g., \( \delta = 18 \) and 51 nm for bcc Fe and hcp Co, respectively) [42]. In this range, changes in coercivity are huge. From large crystal sizes, a reduction of this parameter enhances the impingement effect of crystal boundaries on the domain wall displacement. However, in the nanometer range, when crystallites are smaller than the wall thickness, averaging out of the magnetocrystalline anisotropy leads to a strong reduction of the coercivity with the sixth power of the crystal size [42]. Therefore, both the softest (\( \alpha \)-Fe nanocrystals embedded in an amorphous FM matrix [42]) and the hardest (FeNdB-based nanocrystalline composites [43]) magnetic materials have nanometer microstructure. The averaging out of the magnetocrystalline anisotropy is effective when the nanocrystals are coupled (normally via a soft magnetic amorphous matrix in which they are embedded).

When ferromagnetic nanocrystals are not coupled, isolated monodomain nanocrystals can exhibit superparamagnetic behavior [44], characterized by a blocking temperature, \( T_B < T_C \). Below \( T_B \), normal FM behavior is observed. However, in the range \( T_B < T < T_C \), the system behaves as a superparamagnet (i.e., a PM with huge magnetic moments and thus described by Langevin function). \( T_B \) depends on the characteristic time of the measuring technique as it is defined as the temperature at which the relaxation time equals this experimental timescale [45]: \( T_B = 25KV/k_B \) in the case of quasi-static measurements, where \( V \) is the volume of the particle.

A general depletion of \( T_C \) is found as crystal size decreases and different models have been proposed to explain this (see some examples in [46]). However, changes in the magnetization and Curie transition are theoretically limited to very few layers, approximately <10, in thin films [47]. Nanosized manganites show a broader transition [48] and even bulk antiferromagnetic manganese can be FM when crystal size is reduced to nanometer scale [49]. Reduction of crystal size from 90 to 38 nm in DyCuAl reduces \( T_C \) from 27 to 24 K [50]. Pr\(_{2}Fe_{17} \) ball milled powders with nanometer size present a lower \( T_C \sim 290 \) K than their bulk counterparts (\( T_C \sim 300 \) K) [51].

Different reasoning affects crystal size effect when a magnetostructural transition occurs. The stabilization of the austenite phase by decreasing of the main grain size has been observed in different Heusler systems produced by rapid quenching [52–54]. Crystal growth and compositional homogenization is enhanced after annealing of these rapidly quenched systems and, generally, increasing the structural and magnetic transition temperatures [55]. Aguilar-Ortiz et al. [56] reported a shift of the martensitic transformation in Ni\(_{50}Mn_{35}In_{15} \) ribbons from 300 to 285 K as the crystal size decreases from 7.3 to 0.9 \( \mu \)m. They also found variations in the Curie transition of both austenite and martensite (from 309 to 293 K and from 199 to 178 K, respectively). On the other hand, a critical grain size below which martensitic transformation is suppressed has been also reported for Ni-Ti [57] and Fe-Pd [58] alloys.

Many production techniques can lead to the formation of a non-perfectly homogeneous system, producing a broadening of the physical properties of the transition with respect to those expected for theoretically pure system. This effect has been reported for La\(_{0.70-x}Eu_xSr_{0.30}MnO_3 \) manganites, where the consequent chemical distribution due to partial substitution of Eu for La affects the magnetic and magnetocaloric properties of the compound [59]. The influence of atomic ordering on the Fe-Zr amorphous powder obtained by high energy ball milling has also been studied, showing that the structural relaxation combined with the homogenization of the composition is responsible for the enhancement of the magnetic interactions [60].

Although the next-nearest-neighbor ordered L2\(_1 \) austenite crystal structure is formed in many kinds of X\(_2\)YZ magnetic Heusler alloys, such as Ni\(_2MnAl \) [61], Mn\(_2NiGa \) [62], and Ni\(_2FeGa \) [63], various locally disordered structures can be found in the L2\(_1 \) matrix. These materials are normally produced.
by melt-spinning technique, which can produce textured polycrystalline ribbons and prevents the formation of additional phases due to the high cooling rates during the fabrication process. However, the crystal structure of these compounds strongly depends on the composition and the quenching rate, which can produce site disorder and will drastically influence the magnetic properties due to the ferromagnetic/antiferromagnetic exchange interaction between atoms on the martensitic transformation. In this sense, Passamani et al. [64] reported that Ni$_{2-x}$Fe$_x$Mn$_{1.44}$Sn$_{0.56}$ alloys show a drastic shift of the martensitic transformation after the replacement of Fe atoms for Ni and/or Mn. In this case, Fe-Mn ferromagnetic interactions compensate Mn-Mn antiferromagnetic ones, which leads to the stabilization of austenite phase. In the case of NiFeGa systems [63], the ferromagnetic character of the sample strongly depends on the Fe-Fe interactions. The presence of Fe antisite atoms on Ni or Ga sites results in the modification of magnetic interactions, changing both $T_C$ and structural transition temperature, $T_t$. For Mn-Ni-Ga Heusler alloys, theoretical studies on ordered and disordered Mn and Ni sites results in $T_C = 958$ K and 425 K, respectively [65]. These values, compared to the experimental one of 588 K, must indicate the existence of a high degree of disorder in this system. In these melt-spun systems, annealing produces an increase of $T_t$, $T_C$, and saturation magnetization compared to those of as-cast alloy [66].

In general, rapidly quenched systems, as commented above, lead to disordering but also to crystal size reduction when crystalline structures are formed. Therefore, both sources may affect the transition temperatures.

Pressure application, linked to cell volume changes, also affects magnetic transitions as the exchange depends on the distance between the interacting atoms. The $T_C$ enhancement of Ni with pressure is reduced for Ni(Fe) alloys with low Fe content. For Ni$_{70}$Fe$_{30}$ alloy, $T_C$ is almost pressure independent. For higher Fe content, $T_C$ decreases with pressure [67].

Pressure application in RECo$_2$ decreases the transition temperature [68] in agreement with the predictions of Khmelevskyi and Mohn [69], which describe the magnetic interaction and order of the transition in these systems taking into account the magnetovolume effects and spin fluctuations. When $0.705 < a < 0.722$ nm, where $a$ is the lattice parameter, itinerant electron metamagnetic transition (FOPT) occurs. For high pressures, the linear decrease of the transition temperature with pressure is lost for RE = Ho and Er, becoming pressure independent above 4 GPa [70]. This has been ascribed to the collapse of the Co magnetic moment sublattice, whereas RE sublattice remains almost unchanged with pressure [71].

Pressure application in La(Fe,Si)$_{13}$ phases decreases the transition temperatures [72]. In fact, the so-called negative pressure effect (addition of interstitial atoms) is particularly important for these magnetocaloric materials and H is added to elevate transition temperatures to room temperature for applications [41].

Theoretical dependence of $T_C$ with pressure for Heusler alloys shows a complex behavior dependent on the composition: e.g., whereas, for (Ni$_{1-x}$Pd$_x$)$_2$MnIn, $T_C$ increases as pressure increases, for (Ni$_{1-x}$Cu$_x$)$_2$MnSn, $T_C$ increases with pressure for $x < 0.7$ but decreases for $x > 0.7$ [73].

3. Effects of Distribution of Transition Temperatures

The most straightforward effect when a DTT occurs is the smearing of the magnetic transition. To show this effect, magnetization curves as a function of temperature and magnetic field, $M(T,H)$, were calculated using AN equation of state (EOS) [13]:

$$H^{1/\gamma} = a(T - T_c)M^{1/2} + bM^{1 + 1/\gamma}$$

(6)

where $a$ and $b$ are prefactors and $\beta$ and $\gamma$ are the critical exponents. Figure 5a shows the obtained curves for different theoretical models (MF, Heisenberg, and Ising). Individual $M_i(T, 0)$ curves were obtained for each contribution to a Gaussian distribution of $T_{C_i}$ characterized by its standard deviation.
$\Delta T_C$ and with an average $\langle T_C \rangle = 300$ K. These conditions for the distribution of $T_C$ are used along this work unless explicitly stated.

Figure 5. (a) Normalized magnetization at zero field vs. temperature calculated using Arrott–Noakes EOS for individual contributions and a Gaussian distribution for several standard deviations. (b) ln($M/M_S$) as a function of ln($\langle T_C \rangle - T$). The slope corresponds to the effective critical exponent $\beta$. Curves were generated using Arrott–Noakes EOS for MF, Heisenberg, and Ising models. The curve corresponding to a single Weiss-type contribution is also shown in the upper panel of (b) as a dotted curve for comparison.

The smearing of the transition necessarily reduces the exponent $\beta$ describing the decay of the magnetization, at zero field, as $T_C$ is approached from lower temperatures: $M \sim (T_C - T)^\beta$. Figure 5b shows this effect for the calculated curves. Close to the transition (where the AN EOS is more reliable), $\beta$ decreases. This could lead to a misinterpretation of the actual parameter of the system when a DTT is neglected. Although for $T_C - T \gg$ the exponent is preserved, it must be taken into account that AN EOS loses its validity far from $T_C$. For example, a single Weiss contribution (dotted curve in upper panel of Figure 5b obtained from Brillouin function) deviates from linearity for $T_C - T > 50$ K.

Magnetocaloric effect (MCE) of different systems were analyzed considering a DTT: amorphous alloys [12,74], SOPT manganites [55,75], and other intermetallic phases [76]. It has been generally reported that the presence of a DTT leads to a decrease of the maximum of the magnetic entropy change, $\Delta S_M$. However, as the $\Delta S_M(T)$ peak becomes broader, an enhancement of the refrigerant capacity can be obtained [76,77]. Whether this enhancement is significant will depend on the thermal range at which a high enough $\Delta S_M$ is preserved.
Concerning MCE, the presence of a DTT affects the exponent $n$ describing the field dependence of $\Delta S_{M_{\text{peak}}}^M(H) = \Delta S_{M_{\text{peak}}}^{\text{ideal}}(\mu_0 H)^n$ at the peak temperature. This parameter is related to the critical exponents $(\beta, \gamma, \delta)$ describing the transition in SOPT pure systems [78]:

$$n = 1 + \frac{\beta - 1}{\beta + \gamma} = 1 + \frac{1}{\delta} \left( 1 - \frac{1}{\beta} \right)$$  \hspace{1cm} (7)

It has been shown [74,79] that, as $\Delta T_C$ increases, $n$ increases from the theoretical value corresponding to the pure phase towards 1. Although this could be a criterion to estimate $\Delta T_C$, it must be taken with care when there are FM impurities such as $\alpha$-Fe, typically found in La-Fe-Si [80] or Fe-based amorphous [81], as they produce the same effect.

To describe FOPT, two different calculations have been done in this work. In a first approximation, magnetization curves were calculated using BR model [3] to describe magnetoelastic transitions:

$$\frac{M}{M_s} = B y \left[ \frac{2\mu g B}{k_B T} \left( \mu_0 H + \lambda M + \lambda_3 M^3 \right) \right]$$  \hspace{1cm} (8)

where $B y(y)$ is the Brillouin function. Instead of referring to $\lambda_3$ coefficient, the model used refers to parameter $\eta$:

$$\eta = \frac{10}{3} \frac{J^2 (J + 1)^2}{2 J^2 + 2 J + 1} \frac{\lambda}{\lambda} \left( n_v g \mu_B \right)^2$$  \hspace{1cm} (9)

where $n_v$ is the numerical density of magnetic moments. For $\eta < 1$, Equation (8) corresponds to a SOPT $(\eta = 0$ corresponds to Weiss model$)$ and, for $\eta > 1$, it corresponds to FOPT, being $\eta = 1$ the curve corresponding to the tricritical point. Figure 6a shows $M(T, 0)/M_s$ for different values of $\eta$ and $\Delta T_C$ and Figure 6b shows the corresponding $\frac{1}{M_s} \frac{\Delta M}{\Delta T}$ curves. It can be observed that the inflexion point, $T_{\text{inf}}$, shifts to lower temperatures as $\Delta T_C$ increases. This feature is used in the next section.

![Figure 6](image-url)

**Figure 6.** (a) Normalized magnetization at zero field vs. temperature calculated using Bean and Rodbell model for individual contributions and a Gaussian distribution for several standard deviations and values of $\eta$ parameter; and (b) the corresponding $\frac{1}{M_s} \frac{\Delta M}{\Delta T}$ curves.
The second method used here to describe FOPT considers abrupt changes from one low temperature phase (martensite) to a high temperature phase (austenite). Both phases are described by Weiss model with their corresponding magnetic moments and $T_C$ values. This simple approach tries to resemble very fast individual FOPT magnetostructural transformations, characteristic of martensitic transformations. Therefore, $T_C$ of the low temperature phase is named as martensitic Curie temperature, $T_{CM}$, and that of the high temperature phase is named austenitic Curie temperature, $T^{A}_{CM}$. As commented above (see Figure 4), martensitic transformation temperature, $T_t$, is much more sensitive than Curie transitions in Heusler alloys. Therefore, we consider a Gaussian DTT of the martensitic transformation temperatures, with a standard deviation $\Delta T_t$, while $T_{CM}$ and $T^{A}_{CM}$ are considered constant. Figure 7 shows the calculated $M(T, 0)$ curves for different $\Delta T_t$ and different $T_{CM}$ and $T^{A}_{CM}$ values, describing FM to PM, PM to FM, and low magnetization FM to high magnetization FM, respectively.

![Figure 7](image-url)

Figure 7. Magnetization at zero field (normalized with respect to that of pure martensite phase at $T = 0$ K) vs. temperature calculated using abrupt transitions from a low temperature phase (Weiss system with $T_{CM}$) to a high temperature phase (Weiss system with $T^{A}_{CM}$) and a Gaussian distribution for several standard deviations of the martensitic transformation. Specific magnetization at 0 K is taken as 15 emu/g for martensite and 90 emu/g for austenite phases.

4. Models to Determine the Parameters of a Distribution of Transition Temperatures

Some authors have proposed to directly obtain the parameters of the distribution by fitting the zero-field magnetization versus temperature curves assuming a Gaussian distribution of $T_C$ and Weiss model for each individual contribution [82,83]. Besides the non-trivial function for fitting, this direct comparison between the Weiss theory and the experimental results asks for a good description of the system in a wide temperature range by this model.

Bebenin et al. [84] studied the magnetocaloric response of inhomogeneous La$_{0.7}$X$_{0.3}$MnO$_3$ (with X = Ca and Ba) using a theoretical approach based on Landau theory, where the free energy per unit volume can be written as a power series of the magnetization $M$, and adding the external field term:

$$f = \frac{1}{2} \alpha (T - T_C) M^2 + \frac{1}{4} B M^4 + \frac{1}{6} D M^6 - \mu_0 M H \cos(\theta)$$  \hspace{1cm} (10)
where \( a(T - T_C) \), \( B \) and \( D \) are the coefficients of the power series expansion in the Landau approximation. The temperature dependence is only considered for the quadratic prefactor and \( \theta \) is the angle between field and magnetization. Based on a Gaussian distribution of \( T_C \), they proposed the following equation to describe the magnetic entropy change per unit volume, \( \Delta s_M(H) \), at \( T_C \), in SOPT systems:

\[
\Delta s_M^{pk}(H) = -\frac{a}{2} \left( \frac{\mu_0 H}{B} \right)^{2/3} - a\Delta T_C \sqrt{2\pi B}
\]

where \( \Delta T_C \) is the standard deviation of the distribution and effects of demagnetizing field can be ignored when high enough fields are considered. At the tricritical point \( B = 0 \), variations of this parameter lead to a different expression (assuming the standard deviation of \( B \) around 0 is small enough):

\[
\Delta s_M^{pk}(H) = -\frac{a}{2} \left( \frac{\mu_0 H}{D} \right)^{2/5} - 0.411 \sqrt{\frac{a\Delta T_C}{D}}
\]

Figure 5. Experimental \( \Delta s_M^{pk}(H) \) vs. \( T_C \) at \( T = 300 \) K and quantum angular momentum \( j = 7/2 \) with a Landé factor of \( g = 2 \) (characteristic values of Gd) [1]. Although the parameters of Gd have been chosen, this does not represent any serious drawback or lack of generality. In fact, the change in \( \langle T_C \rangle \) does not affect the equations (except for \( \langle T_C \rangle \) too close to zero to significantly truncate the Gaussian DTT). However, there is a certain dependence on \( J \), which is shown in Figure 8 for \( T_{inf}^{Weiss} \). As it can be observed (keeping \( g = 2 \), which is valid for transition metals), the differences are only appreciable for \( \Delta T_C > 25 \) K. In the case of \( T_{inf}^{Weiss} \), a change in \( J \) will only change, in the same factor, the constant \( C \) of each individual \( \chi_{eff} = C/(T - T_C) \) susceptibility contribution to the DTT and thus no effect is expected for Equation (15).

Experimentally, \( T_{inf} \) and \( T_X \) can be obtained from the analysis of the approach to saturation of the magnetization curves [85] and are independent of the magnetic field, while \( T_{MCE} \) depends on the maximum applied field (i.e., Equation (14) is obtained for \( \mu_0 H = 1 \) T).

Assuming Arrott–Noakes EOS (using \( a = 1 \) Oe\(^{1/\gamma}/K \) and \( b = -0.01 \) Oe\(^{1/\gamma}/(\text{emu/g})^{1/\gamma-1/\beta} \)) to describe the systems, similar equations to Equations (13) and (15) can be obtained. Those for \( T_{inf} \) derived from the calculations shown in Figure 5 result:

\[
T_{inf}^{MF} - \langle T_C \rangle = -0.770(5)\Delta T_C
\]
\[ T_{\text{Heisenberg}}^{\text{inf}} - \langle T_C \rangle = -0.529(4) \Delta T_c \] (17)

\[ T_{\text{Ising}}^{\text{inf}} - \langle T_C \rangle = -0.461(5) \Delta T_c \] (18)

Figure 8. Deviations of \( T_{\text{Weiss}}^{\text{inf}} \) with respect to \( \langle T_C \rangle \) as a function of \( \Delta T_c \) for different values of \( J \).

Figure 9a shows the calculated \( \chi_P \) curves as a function of temperature for these three set of critical exponents in AN EOS and Figure 9b shows the evolution of the peak temperature with \( \Delta T_c \). The equations derived from the fitting are:

\[ T_{\chi}^{\text{MF}} - \langle T_C \rangle = 0.489(18) \Delta T_c - 0.0034(4) \Delta T_c^2 \] (19)

\[ T_{\chi}^{\text{Heisenberg}} - \langle T_C \rangle = 0.285(19) \Delta T_c - 0.0027(5) \Delta T_c^2 \] (20)

\[ T_{\chi}^{\text{Ising}} - \langle T_C \rangle = 0.377(22) \Delta T_c - 0.0036(4) \Delta T_c^2 \] (21)

Figure 9. (a) \( \chi_P \) curves as a function of temperature for MF, Heisenberg, and Ising systems for different values of \( \Delta T_c \). (b) Peak temperature of \( \chi_P \) as a function of \( \Delta T_c \).
Concerning calculations derived from BR model, Figure 10 shows the $\eta$ dependence of the slope of $T_{inf} - \langle T_C \rangle$ vs. $\Delta T_C$. A quadratic dependence is observed for values describing SOPT. The following equation can be derived for SOPT:

$$T_{inf}^{BR}(\eta) - \langle T_C \rangle = \left[-0.730(3) + 0.218(21)\eta + 0.188(22)\eta^2\right]\Delta T_C$$  \hspace{1cm} (22)

In the case of FOPT, the difference becomes constant for $\eta > 1.5$ ($T_{inf}^{BR}(\eta) - \langle T_C \rangle \sim -0.15$).

In the $\eta$ range corresponding to SOPT, magnetic transition of each individual contribution to DTT occurs at its $T_{ci}$ and thus Equation (15) holds and $T_{inf}^{BR}(\eta < 1) = T_{x}^{Weiss}$. However, for FOPT ($\eta > 1$) the magnetic transitions of each individual contributions are shifted to higher temperatures than their corresponding $T_{ci}$ in the DTT and $T_{inf}^{BR}(\eta > 1) \neq T_{x}^{Weiss}$. As $\eta$ increases in this range, the deviation from linearity increases.

![Figure 10](image1)

**Figure 10.** Dependence on $\eta$ of the slope of the plot of $T_{inf}^{BR} - \langle T_C \rangle$ vs. $\Delta T_C$. The parabolic curve is a fitting to the SOPT range.

Finally, concerning our simple model for magnetostructural transitions (magnetization shown in Figure 7), the change in the inflexion point, $T_{inf}^{FOPT}$, depends on the Curie temperature of the FM phase. For high enough values of that $T_{C}$, $T_{inf}^{FOPT} \sim \langle T_I \rangle$, as shown in Figure 11.

![Figure 11](image2)

**Figure 11.** Evolution of $T_{inf} - \langle T_I \rangle$ for simulated curves corresponding to magnetostructural sharp transitions vs. the standard deviation $\Delta T_I$ of DTT and as a function of (a) $T_{Ci}$ in a PM to FM transition; (b) $T_{C1}$ in a FM to PM transition; and (c) $T_{C2}$ in a FM to FM transition. $\langle T_I \rangle = 300$ K for all DTT.

In this FOPT model, the study of $\chi_p$ is senseless except for the transition from a FM low temperature martensite to a PM high temperature austenite. Figure 12a shows two examples of $\chi_p(T)$ for this
type of transition along with the evolution of $T_x$ as a function of $T^A_C$ and $\Delta T_I$ (Figure 12b). This plot (Figure 12b), in combination with Figure 11b, can be used to estimate the parameters of the DTT. However, for those transitions with a FM phase above $T_I$, a rough estimation of the DTT parameters could be obtained by fitting the $dM/dT$ curves to a Gaussian function (assuming Curie temperatures are far away from the martensitic transition).

![Figure 12](image)

Figure 12. (a) Calculated $\chi_P$ curves assuming a distribution of sharp FOPT from a FM martensite to a PM austenite for $T^A_C = 50$ K and for $T^A_C = 200$ K. (b) Evolution of the peak temperature of the susceptibility curves vs. $\Delta T_I$ and as a function of $T^A_C$ ($T_I = 300$ K was used for all DTT.

5. Experimental Test of the Proposed Model

To test the proposed model for determining the parameters of the DTT, two different series are used: mechanically alloyed partially amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ alloys and half-Heusler MnCo$_{0.8}$Fe$_{0.2}$Ge intermetallics developed after annealing of a precursor amorphous system. Microstructure of the samples was characterized by X-ray diffraction (XRD). Details on their production and microstructural and magnetic characterization can be found in [86,87] for the amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ alloys and, for the MnCo$_{0.8}$Fe$_{0.2}$Ge intermetallics, in [88].

To apply the different equations (e.g., for Weiss systems, Equations (13)–(15)), magnetization curves are needed. From the analysis of the approach to saturation curves, $T_{mf}$ and $T$ are obtained (a linear approach is used for simplification). Moreover, to obtain $T_{MCE}$, magnetic entropy curves are calculated from thermomagnetic dependence of magnetization using Maxwell thermodynamic relation:

$$\Delta S_M(T) = -\int_0^{H_{max}} \mu_0 \frac{\partial M(T,H)}{\partial T} dH$$

(23)

As expected from Equation (23), $T_{MCE}$, the temperature for the maximum $\Delta S_M$, depends on the maximum applied field $H_{max}$. This value was set to 1 T, as it was done for all the calculations presented above. Magnetization measurements were performed in a Lakeshore 7407 vibrating sample magnetometer. $\Delta S_M(T)$ curves were obtained using the Magnetocaloric Effect Analysis Program [89] to the magnetization curves.

5.1. Partially Amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ Mechanically Alloyed Systems

As a first example, we have applied the previously described method based on the shift of peak temperatures in the frame of the Weiss model (Equations (13)–(15)) to a series of partially amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ alloys. Figure 13a shows the XRD patterns of several partially amorphized samples (the fraction of $\alpha$-Fe crystalline phase, $X_C$, obtained from Mössbauer spectrometry [81,86,87] for each sample is indicated). Figure 13b shows, as an example, the $M(T,H)$ curves of a Fe$_{75}$Nb$_{10}$B$_{15}$ alloy with $X_C = 15\%$. As the magnetic transition studied in this alloy corresponds to the Curie transition of the amorphous phase, effects such as crystal size can be discarded to be responsible of the
presence of a DTT. Therefore, compositional heterogeneities can be considered. As crystalline fraction increases, the geometrical distribution of the amorphous phase would resemble a porous sponge-like configuration with the nanocrystals in the pores.

![Figure 13](image-url)  
Figure 13. Experimental results of partially amorphous Fe$_{75}$Nb$_{10}$B$_{15}$ alloys. (a) XRD patterns as a function of the crystalline fraction (shown in percent). (b) Magnetization curves for different temperatures for the sample with $X_C = 15\%$.

Figure 14a shows the $dM/dT$ at $\mu_0H = 0$ T and the $\chi_P$ curves from a linear fitting of the high field magnetization curves along with the $\Delta S_M(T)$ curves (integrated from 0 to $\mu_0H = 1$ T) for samples with different values of $X_C$.

![Figure 14](image-url)  
Figure 14. (a) Experimental data for $dM/dT$ and $\chi_P$ vs. $T$ curves from the analysis of approach to saturation and $\Delta S_M(T)$ curves for Fe$_{75}$Nb$_{10}$B$_{15}$ partially amorphous alloys as a function of the crystalline fraction (shown in percent in the legend). (b) Experimental peak temperatures for $dM/dT$, $\chi_P$, and $\Delta S_M(T)$ curves (upper panel); mean Curie temperatures, $\langle T_C \rangle$ (middle panel); and standard deviation, $\Delta T_C$, (lower panel) of the DTT from Equations (13)–(15), as a function of the crystalline fraction.
Figure 14b (upper panel) shows the dependence of the different experimental peak temperatures as a function of $X_C$. From these experimental data, the parameters of the DTT, $\langle T_C \rangle$, and $\Delta T_C$ can be obtained applying Equations (13)–(15) for each sample. $\langle T_C \rangle$ is shown in the middle panel of Figure 14b and $\Delta T_C$ in the lower panel of Figure 14b as a function of $X_C$.

Two set of results can be obtained either using Equation (13) combined with Equation (15) or using Equations (14) and (15). Both practical combinations yield the same $\langle T_C \rangle$ values (between the error bars) and it is clear that, as milling time increases and $X_C$ decreases, $\langle T_C \rangle$ increases. This is due to the progressive increase in Fe content in the amorphous matrix (in agreement with the general case shown in Figure 1) as the $\alpha$-Fe crystallites disappears.

Concerning $\Delta T_C$, this parameter does not show a clear trend due to the large relative error bar. However, when $\Delta T_C$ is represented as a function of $\langle T_C \rangle$ (Figure 15), excluding the extreme data ($X_C \leq 2\%$ and $X_C = 68\%$), a certain correlation between both magnitudes could be inferred. As milling progresses and $X_C$ decreases, the DTT describing the amorphous phase would become broader. This can be understood after considering the compositional profile of Nb in Fe-based nanocrystalline systems, where Nb piles up at the boundary of nanocrystals [90]. Therefore, a higher $X_C$ implies closer nanocrystals. This leads to a larger overlapping between the compositional profiles and yields a thinner compositional distribution, implying a smaller $\Delta T_C$. This is schematically described in Figure 16.

Figure 15. $\Delta T_C$ versus $\langle T_C \rangle$ using Equations (13) and (15) (black squares) and Equations (14) and (15) (red circles) for Fe$_{75}$Nb$_{10}$B$_{15}$ partially amorphous alloys. Extreme data for $X_C \leq 2\%$ and $X_C = 68\%$ are excluded.

Figure 16. Schematic view of the broadening of the amorphous compositional profile dependence with the crystalline fraction. Solid red lines correspond to the total compositional profile, whereas dashed black lines correspond to the compositional profiles for isolated nanocrystals.
Differences between average values of $\Delta T_C$, $\langle \Delta T_C \rangle$, obtained using $T_{inf}$ ($\langle \Delta T_C \rangle = 31 \pm 6$ K) and using $T_{MCE}$ ($\langle \Delta T_C \rangle = 32 \pm 5$ K) are smaller than the error bar. It is worth mentioning that the experimental value of the field exponent of $\Delta S^p_k$ (after correcting impurities and demagnetizing field), $n = 0.757 \pm 0.012$ [81], is clearly above 0.67 (the theoretical value for a Weiss model). From [74], a $\Delta T_C \sim 20$ K can shift $n$ from 0.67 to ~0.8, for MF models.

5.2. Half-Heusler MnCo$_{0.8}$Fe$_{0.2}$Ge Intermetallics

MnCo$_{0.8}$Fe$_{0.2}$Ge intermetallics were obtained from controlled crystallization of a mechanically amorphized alloy, which was produced after 50 h of milling. Figure 17a shows the XRD patterns of samples heated at 20 K/min in argon up to the different indicated temperatures. Figure 17b shows the crystal size and the lattice parameters of the crystalline phase as a function of the annealing temperature. XRD results were analyzed by Rietveld fitting (Goodness of fit below 1.8). The samples are single phase and the crystal size increases as annealing temperature increases. Figure 18 shows, as an example, the magnetization curves at different temperatures for a MnCo(Fe)Ge sample heated up to 723 K at 20 K/min.

![Figure 17. (a) XRD patterns of the MnCo$_{0.8}$Fe$_{0.2}$Ge intermetallics milled for 50 h and heated up to the indicated temperatures at 20 K/min. (b) Crystal size (above) and lattice parameters (below) from XRD Rietveld analysis as a function of the annealing temperature.](image1)

![Figure 18. Isothermal magnetization curves for the MnCo(Fe)Ge sample annealed at 723 K.](image2)
Figure 19a shows the $dM/dT$ at $\mu_0H = 0$ T, the $\chi_P$, and the $\Delta S_M(T)$ curves for samples obtained after heating at different temperatures (indicated in the legend) at 20 K/min. Crystallization of the amorphous phase produced by mechanical alloying occurs at ~550 K. Above this temperature, the only change in the microstructure between the different samples is the crystal size, which almost linearly increases from 14 to 38 nm with the heating temperature in the explored range [91].

No clear trend is observed in the experimental peak temperatures (Figure 19b, upper panel) with the annealing temperature of the different samples (i.e., with the crystal size) being the differences smaller than the error bars. However, a clear difference between $T$ and the other two experimental values indicates the existence of a DTT. The estimate average value $\langle \Delta T_C \rangle \sim 10$ K (using both $T_{\text{inf}}$ and $T_{\text{MCE}}$) does not show any trend with the experimental crystal size. $T_C$ can be tailored in these compositions by changing the Fe content [92,93], which could be the source of the DTT. This value is clearly smaller than that previously found for the amorphous matrix in FeNbB, which is in agreement with a more restricted composition in the crystalline phase. Moreover, as there is no dependence on the crystal size, the presence of a crystal size distribution can be discarded as responsible for the existence of the DTT.

Concerning the parameters of the DTT in the frame of Weiss model (Figure 19b, middle and lower panels), the differences between using Equation (13) in combination with Equation (15) and the results using Equations (14) and (15) are smaller than error bars.

The experimental values of $n$ could be taken as the slope of a linear fitting of $ln(\Delta S_M^{\text{fit}})$ vs. $ln(H)$ (for $1 \leq \mu_0H \leq 1.5$ T to prevent demagnetizing field effects). However, the average over the different samples is $n = 0.799 \pm 0.015$, much higher than those expected for pure phases, which agrees with the existence of a DTT. In fact, taking into account Equation (11), the exponent of a pure phase $n_{\text{pure}}$...
cannot be directly obtained by a linear fitting of $\ln(\Delta S_{pk}^{M})$ vs. $\ln(H)$ when a DTT exists, as there is an extra term proportional to $\Delta T_C$. When this fact is taken into account, an average value over the different half-Heusler samples yields $n_{pure} = 0.65 \pm 0.04$, which is in the range of values corresponding to Weiss model.

6. Conclusions

During the production of experimental samples, the presence of compositional inhomogeneities, disordering, and distribution of crystal sizes or stress fields can lead to the presence of a distribution of transition temperatures (DTT). Concerning those transitions implying a change in the magnetic properties of the system, the presence of a DTT leads to deviations from the predictions derived from models of pure single phases. In this work, some of these effects are summarized.

From the study of the temperature dependence of the approach to saturation curves, saturation magnetization and paramagnetic susceptibility can be experimentally obtained. The shift of the peak temperatures of these two magnitudes has been analyzed for different model systems (Weiss, Heisenberg, Ising, and Bean and Rodbell) and we have proposed a set of equations to estimate the parameters of the DTT from these shifts.

The results were applied to two different series of alloys, partially amorphous Fe-Nb-B and MnCo(Fe)Ge half-Heusler alloys, for which a mean field model describes the experimental data. It is pointed that the proposed equations depend on the assumed model but the study of the variation of other magnetic properties, such as the magnetocaloric effect, could help to elucidate the most appropriate model to describe our system.


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References


23. Fang, Y.K.; Chen, H.C.; Hsieh, C.C.; Chang, H.W.; Zhao, X.G.; Chang, W.C.; Li, W. Structures and magnetocaloric effects of Gd₆₅₋ₓREₓFeₓAl₁₅ (x = 0–20; RE=Tb, Dy, Ho, and Er) ribbons. J. Appl. Phys. 2011, 109, 07A933. [CrossRef]


27. Wang, Y.; Bi, X. The role of Zr and B in room temperature magnetic entropy change of FeZrB amorphous alloys. Appl. Phys. Lett. 2009, 95, 262501. [CrossRef]

28. Álvarez, P.; Gorria, P.; Sánchez Marcos, J.; Fernández Barquin, L.; Blanco, J.A. The role of boron on the magnetocaloric effect of FeZrB metallic glasses. Intermetallics 2010, 18, 2464–2467. [CrossRef]


32. Wali, M.; Skini, R.; Khlifi, M.; Dhahri, E.; Hilil, E.K. A giant magnetocaloric effect with a tunable temperature transition close to room temperature in Na-deficient La$_{0.8}$Na$_{0.2}$,Cr$_3$MnO$_3$ manganites. *Dalt. Trans.* 2015, 44, 12796–12803. [CrossRef]

33. Szewczyk, A.; Gutowska, M.; Dabrowski, B.; Plackowski, T.; Danilova, N.P.; Gaidukov, Y.P. Specific heat effects in lanthanum-deficiency manganites La$_{0.8-x}$Ca$_x$MnO$_3$ (0.00 $\leq x \leq 0.20$) with a first-order magnetic phase transition. *J. Magn. Mater.* 2014, 364, 5–10. [CrossRef]

34. Regaieg, Y.; Sicard, L.; Monnier, J.; Koubaa, M.; Ammar-Merah, S.; Cheikhrouhou, A. Magnetic and magnetocaloric properties of La$_{0.85}$(Na$_{1-x}$K$_x$)$_{0.15}$MnO$_3$ ceramics produced by reactive spark plasma sintering. *J. Appl. Phys.* 2014, 115, 179A17. [CrossRef]


37. Barik, S.K.; Mahendiran, R. Effect of Bi doping on magnetic and magnetocaloric properties of La$_{0.7-x}$Bi$_x$Sr$_3$MnO$_3$ (0.05 $\leq x \leq 0.40$). *J. Appl. Phys.* 2010, 107, 93906. [CrossRef]


41. Andrade, V.M.; Vivas, R.J.C.; Pedro, S.S.; Tedesco, J.C.G.; Rossi, A.L.; Coelho, A.A.; Rocco, D.L.; Reis, M.S. Magnetic and magnetocaloric properties of La$_{0.6}$Ca$_{0.4}$MnO$_3$ tunable by particle size and dimensionality. *Acta Mater.* 2016, 102, 49–55. [CrossRef]

42. Das, K.; Das, I. Giant enhancement of magnetocaloric effect at room temperature by the formation of nanoparticle of La$_{0.48}$Ca$_{0.52}$MnO$_3$ compound. *J. Appl. Phys.* 2016, 119, 39303. [CrossRef]

43. Andrade, V.M.; Vivas, R.J.C.; Pedro, S.S.; Tedesco, J.C.G.; Rossi, A.L.; Coelho, A.A.; Rocco, D.L.; Reis, M.S. Magnetic and magnetocaloric properties of La$_{0.6}$Ca$_{0.4}$MnO$_3$ tunable by particle size and dimensionality. *Acta Mater.* 2016, 102, 49–55. [CrossRef]


60. Lyubina, J.; Nenkov, K.; Schultz, L.; Gutfeld, O. Multiple Metamagnetic Transitions in the Magnetic La(Fe$_{0.9}$Si$_{1.1}$)$_2$H$_x$. *Phys. Rev. Lett.* 2008, 101, 177203. [CrossRef]


75. M’Nassri, R.; Cheikhrouhou-Koubaa, W.; Koubaa, M.; Boujdada, N.; Cheikhrouhou, A. Magnetic and magnetocaloric properties of Pr$_{0.6}$Eu$_{0.4}$Sr$_{0.4}$MnO$_3$ manganese oxides. *Sol. Stat. Comm.* 2011, 151, 1579–1582. [CrossRef]


77. Blázquez, J.S.; Franco, V.; Conde, A. Enhancement of the magnetic refrigerant capacity in partially amorphous Fe70Zr30 powders obtained by mechanical alloying. *Intermetallics* 2012, 26, 52–56. [CrossRef]


81. Ipus, J.J.; Moreno-Ramírez, L.M.; Blázquez, J.S.; Franco, V.; Conde, A. A procedure to extract the magnetocaloric parameters of the single phases from experimental data of a multiphase system. *Appl. Phys. Lett.* 2014, 105, 172405. [CrossRef]


84. Bebenin, N.G.; Zainullina, R.I.; Ustinov, V.V. Magnetocaloric effect in inhomogeneous ferromagnets. *J. Appl. Phys.* 2013, 113, 73907. [CrossRef]


88. Vidal-Crespo, A.; Ipus, J.J.; Blázquez, J.S.; Conde, A. Mechanical Amorphization and Recrystallization of Mn-Co(Fe)-Ge(Si) Compositions. *Metals* 2019, 9, 534. [CrossRef]


