STRUCTURAL AND MAGNETIC PROPERTIES OF Sm$_2$Fe$_{17-x}$Co$_x$ POLYCRYSTALLINE COMPOUNDS WITH $0 \leq x \leq 3$

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ABSTRACT: Samples of Sm$_2$Fe$_{17-x}$Co$_x$ ($x = 0.5 - 3$) were prepared by arc-melting and subsequently annealed at a temperature 1225 K, were studied by X-ray diffraction (XRD), using the Rietveld method, coupled to Curie temperature $T_c$ measurements. The as prepared compounds crystallize in a rhombohedral structure Th$_2$Zn$_{17}$-type. The Curie temperature increases linearly with "x" to reach 790 K for $x = 3$. The increase of $T_c$ despite the low contraction of the cell volume can be explained by the strong exchange integrals $J_{Co-Co}$ and $J_{Fe-Co}$. The substitution of Co was assumed to contribute to complete the 3d sub band, reduce the negative interactions and induce the Curie temperature enhancement.

Key words: Rare earth compounds, Transition metal compounds, Crystal structure, Magnetic measurements.

INTRODUCTION

The R$_2$Fe$_{17}$ compounds, where R is rare-earth element, are known as the most iron rich of all the binary rare earth intermetallics. Although their high saturation magnetization, the relatively low Curie temperature and easy plane magnetocrystalline anisotropy at room temperature restrict the possible application of these materials as permanent magnets [1]. It was shown that the Curie temperature can be improved by replacement of Fe by Al, Si, Ga [2], Mn [3], Zr[4] and Cr [5]. The saturation magnetization as well as the Curie temperature of the R$_2$Fe$_{17}$ compounds could be improved by substitution of Fe by Co. However, only few works deal with cobalt contents [6-9].

The carbon insertion dramatically increases the Curie temperature of the R$_2$Fe$_{17-x}$M$_x$Cy compounds [10]. The Curie temperature increases slowly with the Fe atoms were substituted by only Zr or Cr atoms [4, 5]. The insertion of carbon atoms leaves to a significant increase of the $T_c$, which reaches 551 K for Sm$_2$Fe$_{15.5}$Cr$_1.5$C$_2$[10]. The enhancement of the Curie temperature was due to a lowering of the hybridization of the iron atoms with their neighbors, the magnetovolume effect and the reduction of antiferromagnetic interactions. For the compounds (Sm$_{0.7}$Nd$_{0.3}$)(Fe$_{1-x}$Co$_x$) with 0 $\leq x \leq 0.3$, the Curie temperature increases with "$x"$ to reach 836 K for $x = 0.3$ [6].

In this work, in order to understand how the cobalt atoms improved the $T_c$ of the R$_2$Fe$_{17}$ compounds, intermetallic alloys of Sm$_2$Fe$_{17-x}$Co$_x$ ($x = 0.5 - 3$) were synthesized by arc melting and characterized by XRD and magnetic measurements.

EXPERIMENTAL DETAILS

Polycrystalline compounds of formula Sm$_2$Fe$_{17-x}$Co$_x$ ($x = 0.5 - 3$) were prepared by arc melting a mixture of high-purity powders of Sm (99.99 %), Co (99 %) and Fe (99 %) in water-
cooled arc furnace. Melting was done under a high purity argon atmosphere and the alloys were melted several times in order to insure homogeneity. After arc melting, the as cast ingots were put in evacuated (10^-3Torr) quartz tubes and were annealed at 1225 K during 48 h to annihilate the residual stress and the defaults induced by arc melting and the argon quenching.

X-ray diffraction (XRD) measurements were carried out with Cu Kα radiation (λ = 1.5405 Å) on a Brucker diffractometer equipped with a single-crystal graphite monochromator. The XRD patterns were collected with and without an internal etalon (silicon) to have good precision on the lattice parameter values. The data were fitted with the FULLPROF program [13] based on the Rietveld method [14].

The Curie temperatures Tc were measured by a differential sample magnetometer (Manics) in a low magnetic field of 1 kOe. Tc was determined from the M-T curve by extrapolating the linear part of the M-T curve and finding the temperature value of the intersection with the extended baseline.

RESULTS AND DISCUSSION

Figure 1 gives the XRD patterns of the Sm_{2}Fe_{17-x}Co_{x} compounds. Based on this Figure, we notice that for a weak concentration of Co (x = 0.5) a residual phase of α-Fe exists. However, for high Co concentration the Sm_{2}Fe_{17-x}Co_{x} (x = 1-3) compounds are single phase corresponding to the Th_{2}Zn_{17} type rhombohedral structure. Bessais et al. [12] showed that the nanostructured Sm_{2}Fe_{17-x}Co_{x} (x = 0.5-2) compounds crystallize mainly in rhombohedral Th_{2}Zn_{17} type structure with additional phases (<5 %) of Sm_{2}O_{3} et SmO-N. The Co substitution surpressed the formation of α-Fe phase as the Zr substitution does [4, 15]. The addition of 1 % at. of Zr prevents the formation of α-Fe phase[15].

The results of the Sm_{2}Fe_{17-x}Co_{x} (x = 0.5-3) XRD patterns analyses, using the Rietveld method, are given in table 1.

The mean diffraction crystallite size (DCS) of the synthesized Sm_{2}Fe_{17-x}Co_{x} compounds, obtained by fitting the XRD patterns with the Rietveld method, ranges between 30 and 38 µm. This implies that the synthesized materials are polycrystalline.

The amount of the α-Fe residual phase is almost equal to 1.75 wt % for x = 0.5. For x > 0.5, the residual α-Fe phase disappears. Figure 2 gives an example of the XRD fitting using the Rietveld method for the Sm_{2}Fe_{15}Co_{2} compound.

![Figure 1: XRD patterns of the Sm_{2}Fe_{17-x}Co_{x} (x = 0.5-3) alloys](image-url)
Table 1. Crystalline parameters of the Sm$_2$Fe$_{17-x}$Co$_x$ (x = 0.5-3) alloys obtained by analyzing the XRD patterns based on the Rietveld method

<table>
<thead>
<tr>
<th>X</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, Å</td>
<td>8.557</td>
<td>8.553</td>
<td>8.550</td>
<td>8.548</td>
<td>8.542</td>
<td>8.542</td>
</tr>
<tr>
<td>c/a</td>
<td>1.455</td>
<td>1.455</td>
<td>1.455</td>
<td>1.455</td>
<td>1.455</td>
<td>1.455</td>
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<td>V, Å$^3$</td>
<td>788.82</td>
<td>787.89</td>
<td>787.156</td>
<td>786.535</td>
<td>785.115</td>
<td>785.115</td>
</tr>
<tr>
<td>% Co, 6c</td>
<td>25</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>% Co, 18h</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8.33</td>
<td>16.66</td>
</tr>
<tr>
<td>R$_B$-factor</td>
<td>10.48</td>
<td>9.64</td>
<td>10.55</td>
<td>8.65</td>
<td>10.52</td>
<td>8.96</td>
</tr>
<tr>
<td>R$_F$-factor</td>
<td>8.10</td>
<td>7.82</td>
<td>8.63</td>
<td>7.12</td>
<td>9.36</td>
<td>6.99</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.11</td>
<td>2.70</td>
<td>2.64</td>
<td>2.17</td>
<td>2.18</td>
<td>2.36</td>
</tr>
<tr>
<td>% α-Fe</td>
<td>1.75</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mean diffraction crystalline size, µm</td>
<td>38</td>
<td>35</td>
<td>36</td>
<td>30</td>
<td>37</td>
<td>33</td>
</tr>
</tbody>
</table>

Figure 3 shows the variations of the lattice parameters “a” and “c” of the Sm$_2$Fe$_{17-x}$Co$_x$ compounds as a function of the Co content “x”. In all the substitution field, the lattice parameters “a” and “c” decrease when increasing the Co content “x”. This decrease is due to the fact that the Co atomic radius (r$_{Co} = 1.25$ Å) is less than the Fe one (r$_{Fe} = 1.26$ Å). The decrease of lattice parameters “a” and “c” causes the decrease of the unit cell volume “V” (Figure 4). The constant value of the c/a ratio (Table1) suggests that the unit cell volume compression is isotropic.

In the 2:17 crystalline lattice, the Fe atoms occupy the 6c, 18 h, 18 f and 9d sites. The best values of the fit quality parameters (R$_B$-factor, R$_F$-factor and $\chi^2$) of the XRD were obtained when the Co atoms occupied the 6c sites if x ≤ 2 and the 18 h sites if x > 2. The Wigner-Seitz volumes of
the Fe sites, 6c, 18h, 18f and 9d at 293 K are respectively equal to 12.41, 11.99, 11.75 and 11.22 Å³[12]. Based on these values, we think that the Co atoms substitute the Fe atoms in decreasing order of their Wigner-Seitz volumes. Initially, the Co atoms substitute the Fe atoms in the 6c sites until their saturation for x = 2, then the Co atoms substitute the Fe atoms localized in the 18h sites for 2 < x ≤ 3. Figure 5 gives the Curie temperature variation of the Sm₂Fe₁₇₋ₓCoₓ compounds as a function of the Co content “x”. We notice that the Curie temperature increases with “x”. For x = 3, Tc reaches a value of 790 K. A similar behavior has also been found for Sm₂Fe₁₇₋ₓCoₓ compounds prepared by mechanical alloying [12].

Figure 3: Variation of the lattice parameters “a” and “c” as function of the Co content “x”

Figure 4: Variation of unit-cell volume ‘V’ as function of the Co content ‘x’

Figure 5: Variation of the Curie temperature as function of the Sm₂Fe₁₇₋ₓCoₓ ‘x’
Li and Morrish [16] have studied the variation of the Curie temperature of $\text{Sm}_2\text{Fe}_{17}$ as function of the global exchange integrals of all the Fe-Fe couples in $\text{Sm}_2\text{Fe}_{17}$. The exchange integral for a Fe-Fe couple is a function of the distance between the Fe atoms. The results obtained by the authors [16] show that when the interatomic distance is less than 2.45 Å, the exchange interaction between the Fe-Fe pair is negative. Nevertheless, when Fe atoms are located at larger distance, this exchange integral becomes positive. In the $\text{Sm}_2\text{Fe}_{17}$ lattice, as only the Fe(6c) – Fe(6c) and the Fe(9d)-Fe(18f) couples have interatomic distances less than 2.45 Å, they exhibit negative exchange integrals of respectively -201 K and –20 K [16]. This leads to a rather low Curie temperature for the $\text{Sm}_2\text{Fe}_{17}$ compound as this latter is proportional to the $J_{ij}$ exchange integral between the different Fe-Fe couples [17].

Table 2 gives the interatomic distance of the atoms of couples Fe(6c)-Fe(6c) and Fe(9d)-Fe(18h) of the $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_x$ compounds. We remark that the distances between the atoms of these couples decrease with increasing Co content “x”. Nevertheless, despite the decrease of these distances, the $T_c$ of these compounds increases strongly. So, we can deduce that the value of exchange integral of Fe-Fe pair is not only function of the distance between the atoms of the couple but also depends of the chemical nature of the neighbors atoms.

| Table 2: Interatomic distances between the atoms of the different Fe-Fe couples |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | $\text{Sm}_2\text{Fe}_{17}$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_0.5$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_1$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_{1.5}$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_2$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_{2.5}$ | $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_3$ |
| Fe-Fe sites                    | Distance (Å)    | Distance (Å)    | Distance (Å)    | Distance (Å)    | Distance (Å)    | Distance (Å)    | Distance (Å)    |
| 6c – 6c                        | 2.3767          | 2.3754          | 2.3749          | 2.3741          | 2.3729          | 2.3714          | 2.3705          |
| 9d – 18f                       | 2.4405          | 2.4400          | 2.4389          | 2.4380          | 2.4375          | 2.4365          | 2.4355          |
| 9d–18h                         | 2.4744          | 2.4726          | 2.4718          | 2.4710          | 2.4701          | 2.4693          | 2.4684          |
| 18f–18h                        | 2.4993          | 2.4975          | 2.4967          | 2.4958          | 2.4950          | 2.4941          | 2.4932          |
| 18h–18h                        | 2.4850          | 2.4833          | 2.4825          | 2.4817          | 2.4808          | 2.4800          | 2.4792          |

Sabiryanov and Jaswal [17] showed that a low concentration of substitutional impurities such as Ga or Si in $\text{Sm}_2\text{Fe}_{17}$ raises its Curie temperature. Self-consistent spin-polarized electronic-structure calculations are performed and exchange parameters ($J_{ij}$) are derived from first-principles for pure $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17-x}A$ (A = Ga, Si) [16]. The authors [17] stated that the changes in exchange parameters with doping are related to the magnetovolume effect and the lowering of hybridization of the iron atoms. In fact, the densities of states showed that both Ga and Si impurities result in the narrowing of the iron $d$ bands which leads to the increase of the effective exchange parameter, i.e. strengthen exchange interactions [17]. The Monte Carlo calculations of the Curie temperatures, based on the Heisenberg model using realistic exchange parameters obtained from first principles, give results which are in a good agreement with experimental data, except for the $\text{Sm}_2\text{Fe}_{17}$ phase and showed that the enhancement of the Curie temperature with doping by $sp$ elements can be understood in terms of the lowering of the hybridization of the iron atoms with their neighbors and magnetovolume effect [17].

So, we assume that the enhancement of the Curie temperature of $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_x$ compounds, when the Fe atoms were substituted by Co, can be understood as results of the lowering of the hybridization of the iron atoms with their neighbors and consequently the increase of exchange interactions which become more positive.

Moreover, qualitatively, when the Fe $3d$ band is nearly full, it is established that positive interactions dominate. For half-full band, competition exists between negative and positive interactions [18]. The substitution of Co, which contributes to complete the $3d$ subband, reduces the negative interactions and induces the Curie temperature enhancement. On the other hand, the strong exchange integrals $J_{\text{Co-Co}}$ and $J_{\text{Fe-Co}}$, as compared to the $J_{\text{Fe-Fe}}$ ones, will largely account for the $T_c$ enhancement of the $\text{Sm}_2\text{Fe}_{17-x}\text{Co}_x$ compounds.
CONCLUSION

Arc melting and subsequent annealing at 1225 K lead to a continuous and homogeneous substitution of Co for Fe in the $\text{P}\overline{3}m\text{ S}\text{m}_2\text{Fe}_{17}$ compound. The unit cell parameters "a", "c" and V decrease in all the substitution domain. The interatomic distances between the atoms of the Fe(6c)–Fe(6c) and Fe(9d)-Fe(18f) couples show a small decrease. Nevertheless, despite this decrease, the Curie temperature increases strongly with "x" to reach 790 K for $x = 3$. This result shows that the Curie temperature is not only function of the interatomic distances between Fe atoms but depends strongly on the chemical nature of the Fe neighboring atoms.

On the other hand, we state that the substitution of Co, which contributes to complete the 3d sub band, reduces the negative interactions and induces an increase of the Curie temperature.

The strong exchange integrals $J_{\text{Co-Co}}$ and $J_{\text{Fe-Co}}$, as compared to the $J_{\text{Fe-Fe}}$ ones, may also largely account for the Tc enhancement.

RÉFÉRENCES