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STRUCTURAL AND MAGNETIC PROPERTIES OF $Sm_2Fe_{17-x}Co_x$ POLYCRISTALLINE COMPOUNDS WITH $0 \leq x \leq 3$

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ABSTRACT : Samples of $Sm_2Fe_{17-x}Co_x$ (x = 0.5 –3) arc-melted and subsequently annealed at a temperature 1225 K, were studied by X-ray diffraction (XRD), using the Rietveld method, coupled to Curie temperature Tc measurements. The as prepared compounds crystallize in a rhombohedral structure Th_2Zn_{17}-type. The Curie temperature increases linearly with "x" to reach 790 K for x = 3. The increase of Tc 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.

RESUME : Des échantillons de $Sm_2Fe_{17-x}Co_x$ (x = 0.5 –3) préparés par fusion à l'arc suivi d'un recuit à une température de 1225 K, ont été étudiés par diffraction des rayons X (XRD), en utilisant la méthode de Rietveld, couplée aux mesures de la température de Curie. Les composés préparés cristallisent en structure rhomboédrique de type Th_2Zn_{17}. La température de Curie augmente linéairement avec "x" pour atteindre 790 K pour x = 3. L'augmentation de Tc malgré la faible contraction du volume de maille peut être expliqué par les fortes intégrales d'échange J_{Co-Co} et J_{Fe-Co}. La substitution de Co, qui contribue au remplissage des sous couches 3d , réduit les interactions négatives et induit l'amélioration de la température de Curie.

Mots clés: Composés des terres rares, Composés métalliques de transition, Structure cristalline, Mesures magnétiques.

INTRODUCTION

The R_2Fe_{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 magnetocristalline 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_2Fe_{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 $R_2Fe_{17-x}M_xC_y$ (M = Cr, Ga ,Co) alloys [10-12].

The Curie temperature increases slowly when the Fe atoms were substituted by only Zr or Cr atoms [4, 5]. The insertion of carbon atoms leads to a significant increase of the Tc, which reachs 551 K for $Sm_2Fe_{15.5}Cr_{1.5}C_2$[10]. The enhancement of the Tc was due to a lowering of the hybridation 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 Tc of the R_2Fe_{17} compounds, intermettalic alloys of $Sm_2Fe_{17-x}Co_x$ (x = 0.5 – 3) were synthesized by arc melting and characterized by XRD and magnetic measurements.

EXPERIMENTAL DETAILS

Polycrystalline compounds of formula $Sm_2Fe_{17-x}Co_x$ (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-

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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^{-3}Torr) 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 $Sm_2Fe_{17-x}Co_x$ 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 $Sm_2Fe_{17-x}Co_x$ (x = 1-3) compounds are single phase corresponding to the Th_2Zn_{17} type rhombohedral structure. Bessais et al. [12] showed that the nanostructured $Sm_2Fe_{17-x}Co_x$ (x = 0.5-2) compounds crystallize mainly in rhombohedral Th_2Zn_{17} type structure with additional phases (< 5 %) of Sm_2O_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 $Sm_2Fe_{17-x}Co_x$ (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 $Sm_2Fe_{17-x}Co_x$ 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 $Sm_2Fe_{15}Co_2$ compound.

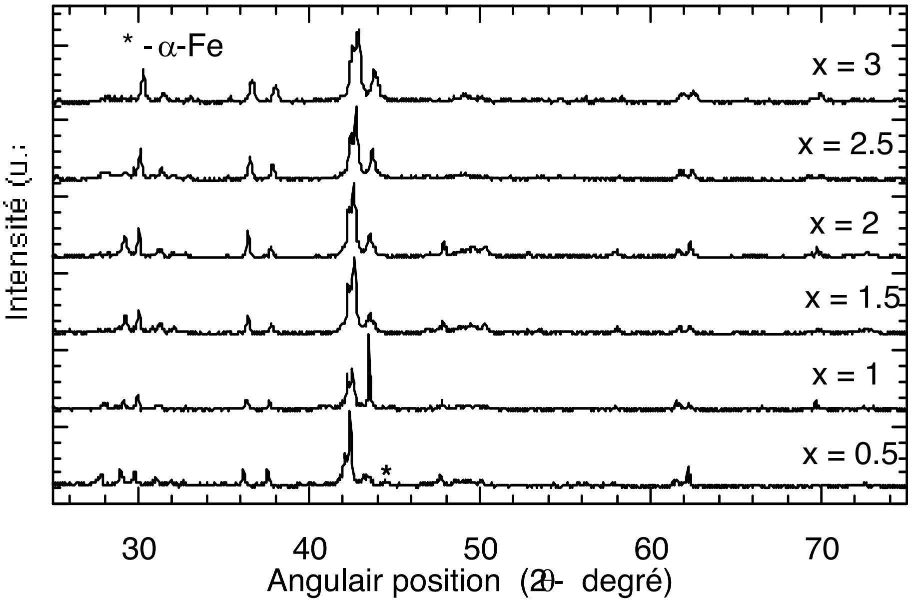

Figure 1: XRD patterns of the $Sm_2Fe_{17-x}Co_x$ (x = 0.5- 3) alloys

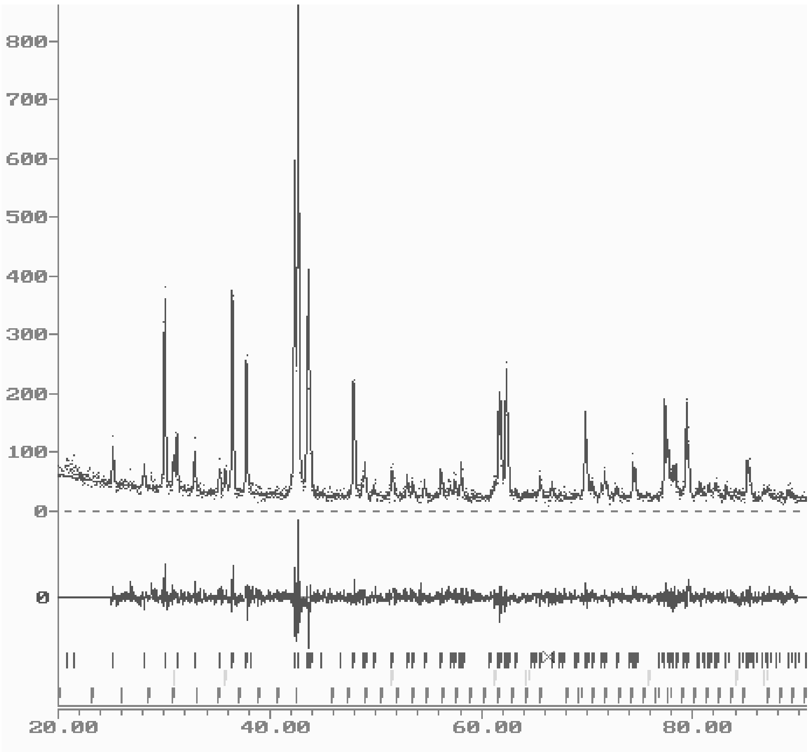

Figure 2 : Example of fitting of the $Sm_2Fe_{15}Co_2$ XRD pattern by use of the Rietveld method

Table 1. Crystalline parameters of the $Sm_2Fe_{17-x}Co_x$ (x = 0.5- 3) alloys obtained by analyzing the XRD patterns based on the Rietveld method

X	**0.5**	**1**	**1.5**	**2**	**2.5**	**3**
a, Å	8.557	8.553	8.550	8.548	8.542	8.542
c, Å	12.453	12.450	12.447	12.443	12.434	12.434
c/a	1.455	1.455	1.455	1.455	1.455	1.455
V, $Å^3$	788.82	787.89	787.156	786.535	785.115	785.115
% Co, 6c	25	50	75	100	100	100
% Co,18h	0	0	0	0	8.33	16.66
R_B- factor	10.48	9.64	10.55	8.65	10.52	8.96
R_F- factor	8.10	7.82	8.63	7.12	9.36	6.99
χ^2	2.11	2.70	2.64	2.17	2.18	2.36
% α-Fe	1.75	0	0	0	0	0
Mean diffraction crystalline size, μm	38	35	36	30	37	33

Figure 3 shows the variations of the lattice parameters “a” and “c” of the $Sm_2Fe_{17-x}Co_x$ 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 χ^2) of the XRD were obtained when the Co atoms occupied the 6c sites if $x \leq 2$ 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 Å^3[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 $2 < x \leq 3$. Figure 5 gives the Curie temperature variation of the $Sm_2Fe_{17-x}Co_x$ 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 $Sm_2Fe_{17-x}Co_x$ compounds prepared by mechanical alloying [12]

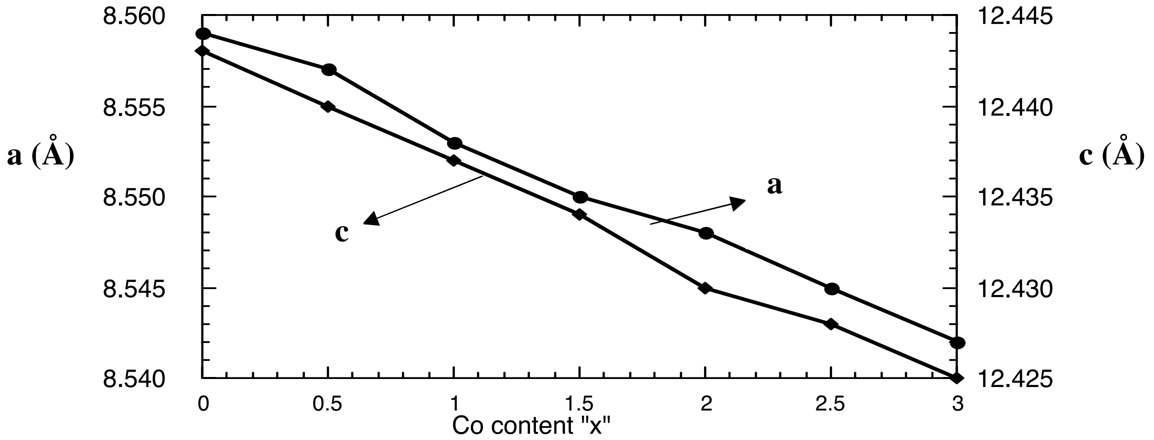

Figure 3: Variation of the lattice parameters ''a'' and ''c'' as function of the Co content ''x''

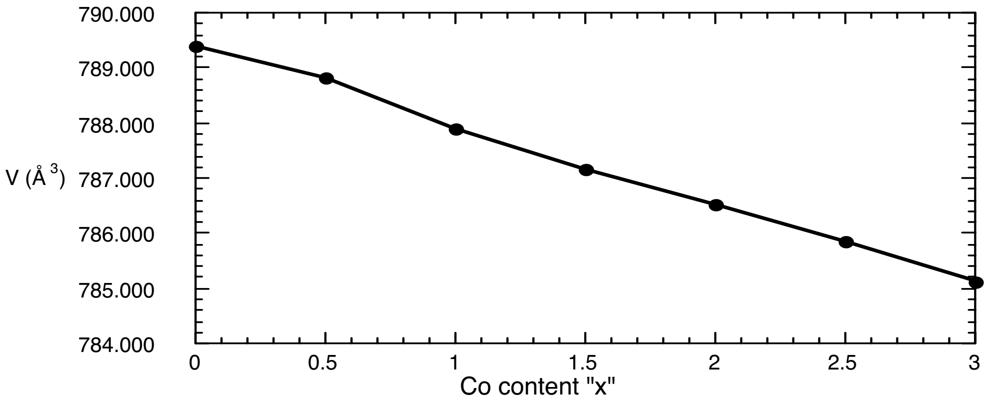

Figure 4: Variation of unit-cell volume 'V' as function of the Co content ''x''

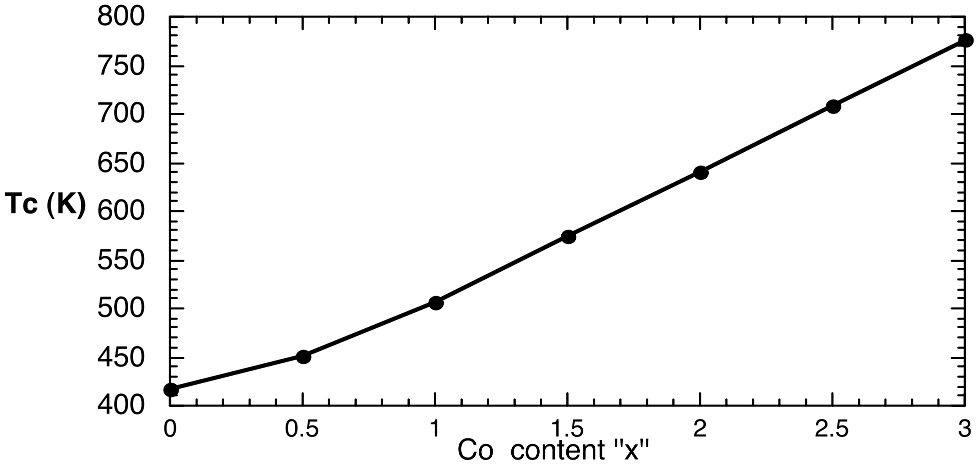

Figure 5 : Variation of the Curie temperature as function of the $Sm_2Fe_{17-x}Co_x$ ''x''

Li and Morrish [16] have studied the variation of the Curie temperature of Sm_2Fe_{17} as function of the global exchange integrals of all the Fe-Fe couples in Sm_2Fe_{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 Sm_2Fe_{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 Sm_2Fe_{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 $Sm_2Fe_{17-x}Co_x$ 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 Tc 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

	Sm_2Fe_{17}	$Sm_2Fe_{16.5}Co_{0.5}$	$Sm_2Fe_{16}Co_1$	$Sm_2Fe_{15.5}Co_{1.5}$	$Sm_2Fe_{15}Co_2$	$Sm_2Fe_{14.5}Co_{2.5}$	$Sm_2Fe_{14}Co_3$
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–18f	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 Sm_2Fe_{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 Sm_2Fe_{17} and $Sm_2Fe_{16}A$ (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 Sm_2Fe_{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 $Sm_2Fe_{17-x}Co_x$ 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_{Co-Co} and J_{Fe-Co}, as compared to the J_{Fe-Fe} ones, will largely account for the Tc enhancement of the $Sm_2Fe_{17-x}Co_x$ compounds.

CONCLUSION

Arc melting and subsequent annealing at 1225 K lead to a continuous and homogeneous substitution of Co for Fe in the $P\bar{3}m$ Sm_2Fe_{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_{Co-Co} and J_{Fe-Co}, as compared to the J_{Fe-Fe} ones, may also largely account for the Tc enhancement.

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