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A MÖSSBAUER EFFECT STUDY ON Co DOPING IN $SmTiFe_{11}$ COMPOUND

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ABSTRACT

A series of $SmTiFe_{11-x}Co_x$ compounds where x ranges from zero to five, have been studied by ^{57}Fe Mössbauer spectroscopy, X–ray diffraction and related magnetic measurements. The radom site occupation of Co atom in $SmTiFe_{11-x}Co_x$ was found when $x \geqslant 1$. The temperature dependence of the magnetic hyperfine field for $SmTiFe_{11}$ and the Co concentration dependence of the magnetic hyperfine field for the samples, $SmTiFe_{11-x}Co_x$ are obtained. Also the Debye temperature of $SmTiFe_{11}$ have been estimated from the experiments.

Keywords: Mössbauer spectroscopy $SmTiFe_{11}$ compound Co doping

1 INTRODUCTION

A variety of high–performance permanent magnet materials, ternary $Re_2Fe_{14}B$, has been produced since 1983[1]. This kind of compounds, however, has some disadvantages such as low Curie temperature, relatively low negative temperature coefficients of the coercive force and its saturation magnetization. Many research groups have tried to search for other new permanent magnet materials to overcome these shortages mentioned above. Recently, this work has focused on pseudobinary $RFe_{12-x}M_x$ compounds with $ThMn_{12}$–type structure.

Cheng *et al*[2] studied the structure and magnetic properties of $SmTiFe_{11}$ and concluded that $SmTiFe_{11}$ has better magnetic properties than those of $Nd_2Fe_{14}B$ in some respects. This paper studies the effect of Co adding in $SmTiFe_{11-x}Co_x$ compounds where x ranges from 0 to 0.8, on the magnetic proporties by means of Mössbauer spectroscopy, X–ray diffraction and related magnetic measurements.

2 EXPERIMENTAL DETAILS

Samples were prepared by conventional arc–melting method. Appropriate amounts

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of the elements of samarium (purity 99 %), iron (purity 99.9 %), titanium (purity 99 %) and cobalt (purity 99 %) were mixed according to the stoichiometric composition $SmTi(Fe_{1-x}Co_x)_{11}$ and melted in argon. In order to remove oxygen as much as possible from the argon atmosphere, a titanium button was melted in the sample chamber before these samples were melted. During melting, the sample buttons were turned over 5–6 times to achieve good homogeneity. After arc–melting the ingots obtained were wrapped in tantalum foil and sealed in a evacuated quartz tube, then were annealed at 850°C for two weeks.

The chemical composition of these samples were tested by a MARK–2 ICE–AES apparatus and a X–650 scanning electron microscope. The results show that the compositions of the samples are almost consistent with nominal stoichiometric compounds. The X–ray measurements for the powdered alloys, $SmTiFe_{11-x}Co_x$, were made at room temperature and $SmTiFe_{11}$ were done at 78 K besides room temperature using a Y–2 type X–ray diffractometer with Co K_α radiation.

The ^{57}Fe Mössbauer absorption spectra were collected at room temperature for $SmTiFe_{11-x}Co_x$ compounds where x from 0.0 to 5.0 and the sample, $SmTiFe_{11}$, at 80 K, 90 K, 150 K, 200 K, using a MS–500 conventional constant acceleration spectrometer with a $^{57}Co/Pd$ source. All of the data were analyzed by least–square MOSFUN method.

The composition dependence of the Curie temperatures T_c and specific magnetizations σ_s for $SmTiFe_{11-x}Co_x$ compounds were obtained by a standard magnetic measurement techniques with a PAR–155 vibrating sample magnetometer and Faraday balance, respectively.

3 RESULTS AND DISCUSSION

The X–ray diagrams of the annealed $SmTiFe_{11-x}Co_x$ alloys were indexed on the basis of tetragonal $ThMn_{12}$ type structure except some impurity phases, α –Fe, $TiFe_2$ and a bit Sm_2Fe_{17} phase which had previously been detected by Cheng *et al.*[2], were observed in $SmTiFe_{11}$ sample. When the Co is introduced, another new phase, TiFeCo solid solution phase, is observed. The result of X–ray diffraction for $SmTiFe_{11}$ at liquid nitrogen temperature was the same as that at room temperature.

The neutron diffraction experiment[3] indicates preferential Ti occupation at 8*i* sites. Information on the average iron neighbors for iron atoms at 8*j*, 8*i* and 8*f* sites and the average Fe–Fe distance has been provided and confirmed by Hu Boping *et al.*[4] and Bushow *et al.*[5], respectively. Evidently, it can also be used to interpret our experimental results for $SmTiFe_{11-x}Co_x$, namely, the hyperfine fields at different iron sites satisfy the relation, $HF_{8i} > HF_{8j} > HF_{8f}$, here HF stands for hyperfine field, the subscripts of HF, 8*i*, 8*j* and 8*f*, represent the respective inequivalent iron sites of

$SmTiFe_{11-x}Co_x$. Such a random iron population in iron nearest-neighbors for 8*f*, 8*i* and 8*j* sites is formed due to the Ti atoms preferential occupation in 8*i* sites that cause a distribution of the hyperfine field for each iron site. The distributions of the hyperfine fields on different iron sites depend upon the different iron nearest neighbor population. On the assumption that the distribution follows a binomial relation, the probability of iron nearest neighbors population can be given by

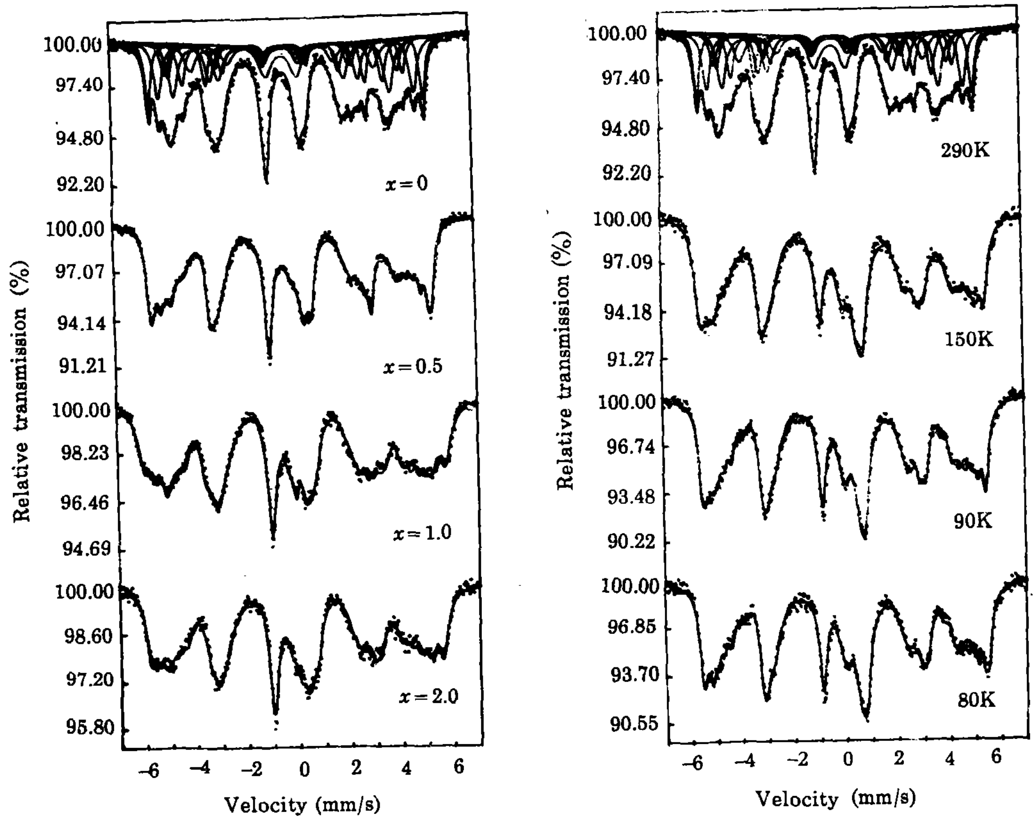

Fig.1 Mössbauer spectra of $SmTiFe_{11-x}Co_x$ at room temperature(*a*) and Mössbauer spectra of $SmTiFe_{11}$ at different temperature (*b*)

$$P^m_n = C^m_n\, x^m\, (1-x)^{m-n}$$

where x is the concentration of Ti atoms, m is the number of Ti atoms populated at a certain site, n is the maximum of iron nearest-neighbors at a certain site. It is evident that each distribution corresponds to each sextet subspectrum of the Mössbauer spectra. In terms of the calculation of the probability for iron neighbors population, the distribution of the hyperfine field was fitted by introducing two subspectra for each site (see Fig.1). Table 1 shows the average hyperfine field at each iron site increases with Co content x, here x from zero to 1. However, for x from 1 to 5 no considerable change is observed. These are in good agreement with the relation between the specific saturation magnetization and the Co concentration obtained by us. Based on Fig.2, the specific saturation magnetization reaches to maximum at Co content, $x=2$. The experimental results can be explained according to the results reported by Ref.[6] which revealed that Co atom located itself in near neighbors of iron atom would increase the hyperfine field with low Co concentration[7] of spin polarization as a function of Co concentration. Furthermore, the hyperfine fields for $SmTiFe_{11}$ at 288 K, 150 K, 90 K and 80 K, increase with the temperature also.

Table 1

Hyperfine parameters of ^{57}Fe nuclei on different Co content for different iron sites

Par.sites	x	0	0.2	0.5	1.0	2.0	5.0
8*i*	IS (mm/s)	-0.0037	-0.047	-0.034	-0.0010	-0.020	-0.0040
	QS (mm/s)	-0.063	-0.020	-0.032	-0.016	-0.026	-0.040
	$\bar{B}$ (T)	29.1	30.7	31.3	33.9	33.6	33.9
	I (%)	27	26	27	34	35	34
8*j*	IS (mm/s)	-0.18	-0.10	-0.19	-0.088	-0.11	-0.062
	QS (mm/s)	-0.030	-0.051	-0.037	-0.097	-0.098	-0.13
	$\bar{B}$ (T)	27.0	29.0	29.2	29.4	29.3	29.5
	I (%)	36.5	35	29.5	28.5	28.4	29.5
8*f*	IS (mm/s)	-0.17	-0.16	-0.17	-0.10	-0.13	-0.12
	QS (mm/s)	-0.053	-0.026	-0.034	-0.097	-0.080	-0.067
	$\bar{B}$ (T)	23.1	24.4	25.3	24.8	25.0	24.9
	I (T)	36.5	39	43.5	37.5	36.6	36.5

IS is relative to α -Fe QS denotes the quadrupole splitting $\bar{B}$ expresses the average hyperfine magnetic fields over the assigned sites I denotes the relative intensity

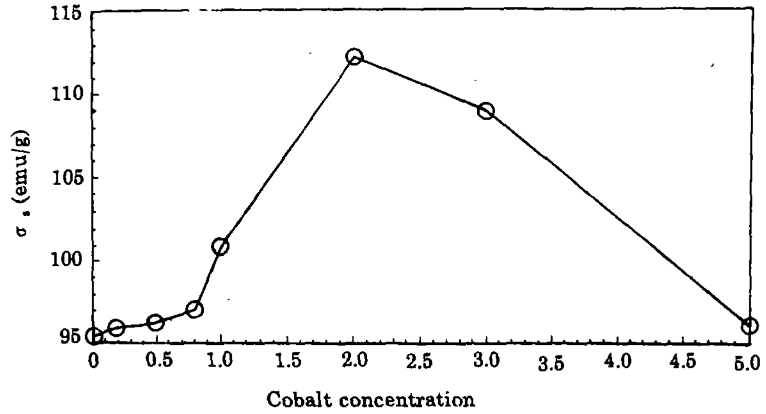

Fig.2 The cobalt concentrations dependence of specific magnetization

Due to Co concentration dependence of relative intensities (Fig.3), we found that the relative intensity for 8*i* site increases about 7 % from $x=0$ to 1. When Co content exceeds 1, the opposite situation appears for 8*j* site, namely the relative intensity decreases about 8 % relative to the same composition range. Thus we can conclude that Co atoms first occupy in 8*j* sites preferentially over the tested composition range. However, as the Co content, *x*, increases continuously, the Co atom will occupy iron sites randomly rather than preferentially.

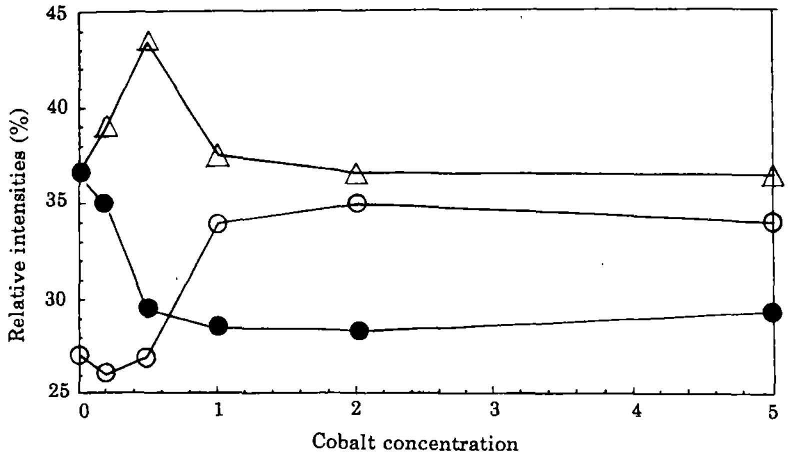

Fig.3 The dependence of the relative intensity on cobalt content

The open and filled circles, and the open triangle denote 8*i*, 8*j* and 8*f* sites, respectively

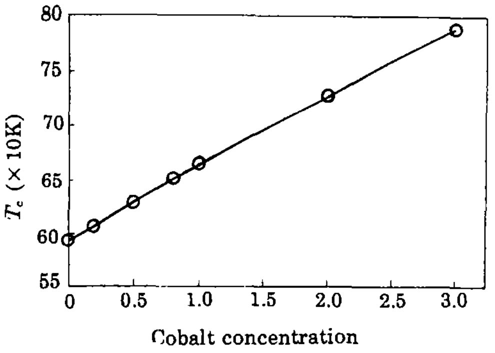

Fig.4 The cobalt concentrations dependence of Curie temperature

In accordance with the results listed in Table 1, we realize that the isomer shifts increase with cobalt content, and this change for 8*i* site is more obvious than 8*j* and 8*f* sites. This indicates the reduction of *d*-electron density for different iron sites due to Co content increase, and the change on *d*-electron density for different iron sites may influence their hyperfine fields. Now we discuss the temperature dependence of the shift of gravity center of the Mössbauer spectrum of SmTiFe$_{11}$. Considering the second Doppler effect, the following relation is given:

$$IS_T = -\langle v^2 \rangle_a / 2c + IS_0$$

where IS_T represents the shift of gravity center of the spectrum, $\langle v^2 \rangle_a$ is the mean-square velocity of iron nuclei in lattice of absorber and IS_0 is the isomer shift. Using the Debye model and making the low temperature approximation, the mean-square velocity has the following relation,

$$\langle v^2 \rangle_a = 9k_B\theta_D / 8M\ [1 + (8\pi^4/15)\ (T/\theta_D)^4]$$

where the k_B is the Boltzman constant, θ_D is the Debye temperature of the material and M is the effective mass of iron nuclei. According to the experimental data at two different temperature, the Debye temperature for $SmTiFe_{11}$ can be roughly estimated about 400 K.

The dependence of the Curie temperature on the Co concentration shows that replacement of Fe by Co leads to a rapid increase of Curie temperature (Fig.4) for Co content being less than unity, and the Curie temperature increases in 70 K per Co atom. Then the Curie temperature slows down gradually, for Co content exceeding 1.

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