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Magnetic Features of $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) Compounds

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The magnetic and thermal properties of the $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) compounds with $0 < x < 3$ have been studied by Magnetic Thermogravimetry (MTG) and Mössbauer Spectroscopy measurements. MTG measurements show that in the M = Mn case Curie temperature increases from T=338 K up to T=341K for $x = 0$ and 0.2 respectively, while $Nd_2Fe_{14}Ga_3$ has a maximum critical temperature of 552 K. The temperature transition decreased with further x increases. On the other hand, the Mössbauer spectrum of the $Nd_2Fe_{14}Mn_3$ exhibits paramagnetic behavior at room temperature and for $Nd_2Fe_{14}Ga_3$a α-Fe phase was detected. In addition, we analyzed the effect of Ga or Mn substitution in Fe sites on the hyperfine field and quadrupole splitting, where these parameters show a different behavior as a result of substitution of Fe by two different ions as Mn or Ga.

Keywords: Rare earth metals and alloys; Fe and its alloys; Mössbauer effect.

Las propiedades térmicas y magnéticas de los compuestos $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) con $0 < x < 3$ han sido estudiadas a través de medidas de Termogravimetría Magnética (MTG) y Espectrometría Mössbauer. Las medidas MTG muestran que en estos compuestos la temperatura de Curie aumenta desde T = 338 K hasta T = 341 K para $x = 0$, $x = 0.2$ respectivamente, en el caso de M = Mn, mientras que $Nd_2Fe_{14}Ga_3$tiene una temperatura critica máxima de 552 K. La temperatura de transición disminuye con el aumento adicional de x. Por otro lado, el espectro Mössbauer del $Nd_2Fe_{14}Mn_3$ exhibe un comportamiento paramagnético a temperatura ambiente y para $Nd_2Fe_{14}Ga_3$ fue detectada una fase de Fe- α. Adicionalmente, analizamos los efectos de la sustitución de Ga o Mn en los sitios de Fe sobre el campo hiperfino y el desdoblamiento cuadrupolar, donde estos parámetros presentan comportamiento diferente como consecuencia de la sustitución de Fe por dos átomos diferentes como son Mn o Ga.

Descriptores: Metales de tierras raras y aleaciones; Fe y sus aleaciones; efecto Mössbauer.

PACS: 71.20.Eh; 75.50.Bb; 76.80.Ty

1. Introduction

In the last years, the R_2Fe_{17}compounds (R = rare earth), have been widely studied, to establish their use as permanent magnets [1,2]. However, their low Curie temperature and absence uniaxial anisotropy near to room temperature have been obstacles to this purpose. Efforts in order to improve these disadvantages are carried out by researchers through substitution with non-magnetic elements such as Al, Ga at the Fe sites [3-5]. This substitution modifies the distances between Fe ions by producing changes at T_c. Attempts for increasing the Curie temperature in $Er_2Fe_{17-x}Ga_x$ using substitution with Ga concentration [5] was conducted by M. Venkatesan in 2000.

Recently, it has been given a special attention to Fe substitution by Mn where antiferromagnetic behavior and big magnetic moment of Mn, can modify Fe sublattice in two ways: expanding lattice and changing magnetic moment [6-10]. The structural effects that produce the increase of x in $R_2Fe_{17-x}M_x$ compounds have been studied to deduce the influence of changes in crystalline parameters on Curie temperature, as was reported for $R_2Fe_{17-x}Mn_x$ (R = Y, Tb) [9]. In the case of Y_2Fe_{17-} a peak was observed in T_c for a concentration $x = 0.3$, while for compounds with Tb, the Curie temperature decreases monotonically when the Mn concentration increases. The decrease of the transition temperature is a result of magnetization decrease of transition metal sublattice. Nd_2Fe_{17} crystallizes in Th_2Zn_{17}-type structure; Fe can occupy 6c, 9d, 18f and 18h positions. The 6c and 18h sites have the most and the least numbers of nearest-neighbor Fe atoms respectively [7]. Thus, it is expected that 6c might be a preferred position by transition metal ions.

Several studies about magnetic behavior of the $Nd_2Fe_{17-x}M_x$, compounds have been reported, most of them have been concentrated into analysis of substitution in order to attain the highest transition temperature and/or coercitive magnetic field. Recently a moderate magneto caloric behavior was observed in these materials. Thus our purpose in the present work is to carry out an analysis of hyperfine parameters near room temperature when Fe ions are replaced by magnetic or non magnetic ions (Mn and Ga respectively) with the objective to determine the magnetocaloric properties for these alloys.

2. Experimental

The $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) compounds were prepared by standard arc melting of high purity elements, 99.5% or better, in a purified argon atmosphere, weight loss was about

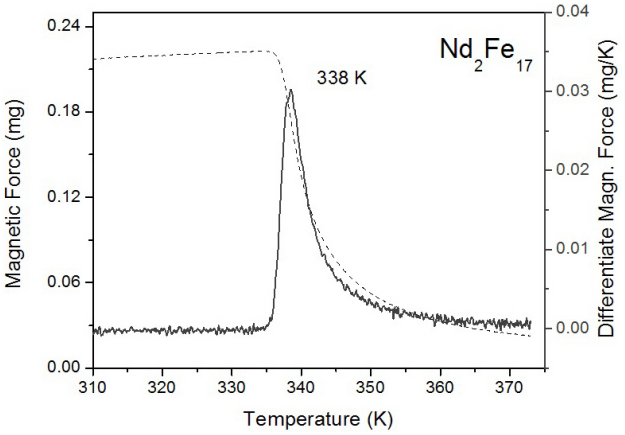

FIGURE 1. Magnetic Force Curve vs Temperature and Differentiate Magnetic Force Nd_2Fe_{17} sample.

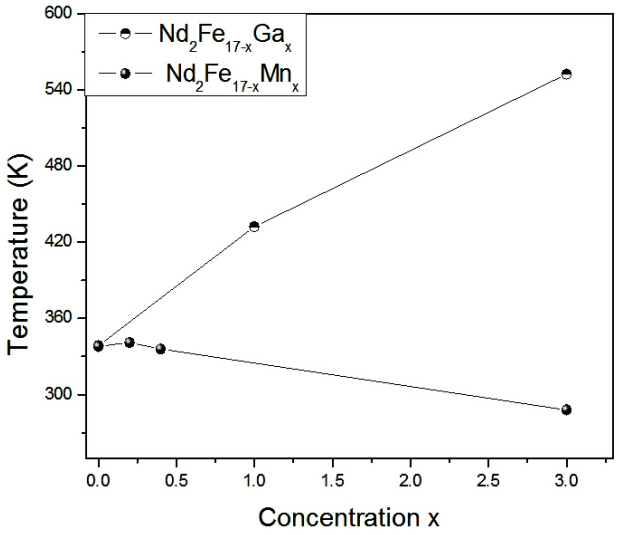

FIGURE 2. Dependence of T_C with the concentration x for $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn), measured with MTG.

6% or less. Then, samples were wrapped in tantalum foil, sealed in an argon-filled quartz tubes, and annealed at 1273 K for 24 hours. Afterwards, samples were fractionated to carry out Magnetic Thermogravimetry and Mössbauer Spectroscopy measurements.

The detection of the phase transition temperature for the ferro/paramagnetic shift was conducted using the Magnetic Thermogravimetric Analysis Technique and through Mössbauer Spectroscopy at room temperature to get information on hyperfine field (B_{hf}) at different sites of iron. Mössbauer Effect measurements at 300 K of $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) compounds, $0<x<3$, were done using a conventional spectrometer with 57-Co/Rh source and α-Fe as calibration sample.

3. Results and discussion

From our MTG measurements we get maximum value of the derivate magnetic force as a function of temperature in $Nd_2Fe_{17-x}M_x$ (M = Ga, Mn) compounds (see Fig. 1). A little increase of temperature with $x = 0.2$ can be observed in the Mn case, while an increase of the x values causes a decrease in the transition temperature. In the Ga case T_c increases as function of x as showed Fig. 2.

The different behaviors of Curie temperature in $Nd_2Fe_{17-x}Ga_x$ and $Nd_2Fe_{17-x}Mn_x$ compounds can be explained by the role of Mn or Ga when one of them substitutes Fe one. Mn and Ga have larger ionic radius than Fe thus expanding the Fe-sublattice, yielding an increase in separation between Fe ions, thus increasing the ferromagnetic character.

In the $Nd_2Fe_{17-x}Mn_x$ case the Curie temperature increases when low concentrations of Mn are added, which can be attributed to the increase in interatomic distance of Fe-Fe ions, giving a ferromagnetic behavior in Fe-sublattice by increase of the ferromagnetic exchange interactions at Fe-6c sites [6,11]. Further increase of Mn concentration intensifies the antiferromagnetic coupling producing a magnetization decrease of the transition metal sublattice [7], as it was evidenced in $Nd_2\ Fe_{14}\ Mn_3$. Since the magnetic transition temperature for this last sample was below room temperature, it was necessary the use of temperature Modulated Differential Scanning Calorimetry technique (MDSC) to detect it due to the absence of a cooling mechanism in the MTG technique (measurement not shown here).

From measurements of Mössbauer effect, the fit of Mössbauer spectra for $Nd_2Fe_{17-x}M_x$(M = Ga, Mn) compounds was conducted through seven independent sextets attributed to the iron sites 6c, $9d_a$, $9d_b$, $18f_a$, $18f_b$, $18h_a$ y $18h_b$, in which the variation of hyperfine parameter; Isomer shift (IS) and quadrupole splitting (QS) were allowed. The sequence in the assignment of the fields assignment for each iron site are $B_{hf}(6c) > B_{hf}(9d) > B_{hf}(18f) > B_{hf}(18h)$. This fact is consistent with preferential site for Fe ions where the most probably site for occupation of transition metal is 6c. Because it was considered the preferential occupation of certain ions for the iron sites, this is in agreement with what was reported by Long in 1994 [3].

It is worth of mention that, in $Nd_2Fe_{17-x}Ga_x$compounds an increase of the average hyperfine field measured at room temperature was observed while increasing the Ga concentration. This fact may be related with the increase of Curie temperature for these compounds. Moreover, the Mössbauer spectrum of $Nd_2Fe_{14}Ga_3$ (see Fig. 3) shows evidence of α-Fe phase, through hyperfine magnetic field measurement of B_{hf} = 330 KOe; this was confirmed by temperature dependence of magnetic force measurements by MTG technique. This non-desired phase could contribute to the increase of both magnetization of compound and its Curie temperature.

In Mössbauer spectrometry measurements of $Nd_2Fe_{17-x}Mn_x$ compounds (see Fig. 4), it was observed that at low Mn concentrations ($x = 0.2$ and $x = 0.4$) an apparent α-Fe phase is shown, however this was discarded later, due to isomer shift (IS) and quadrupole splitting (QS) values did not correspond to the calibration sample; thus it is thought that the compound has sites where the iron is diluted

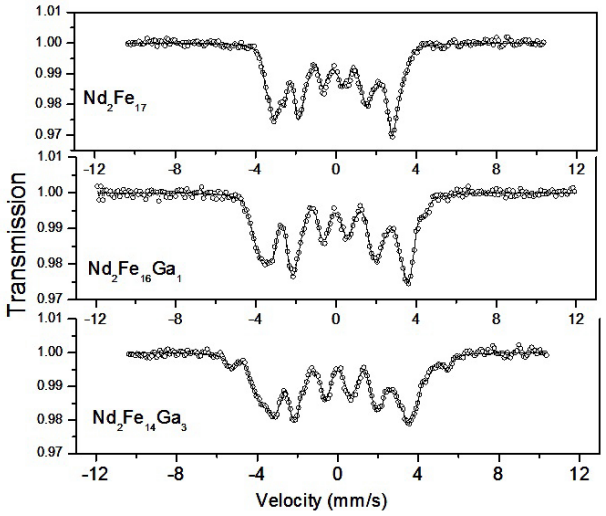

FIGURE 3. Mössbauer Spectra of $Nd_2Fe_{17-x}Ga_x$ at 300 K

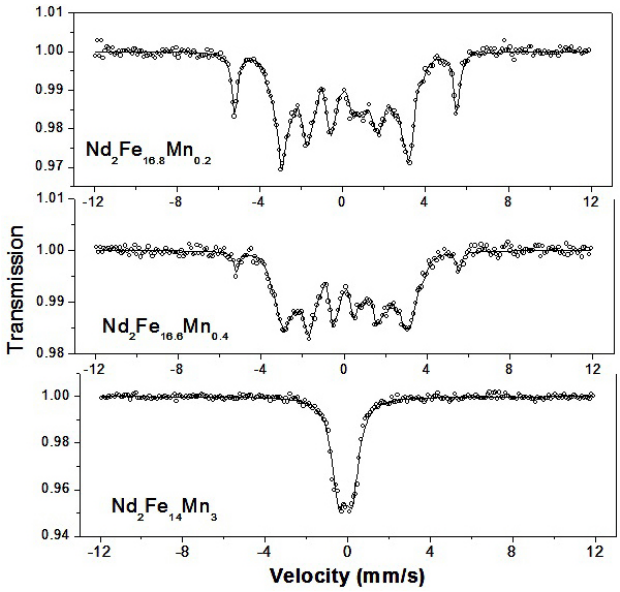

FIGURE 4. Mössbauer Spectrum of $Nd_2Fe_{17-x}Mn_x$ at 300 K

in the trigonal phase appearing as non-pure Fe clusters, and therefore their parameters did not match with the IS and QS values of the calibration sample. In Mössbauer spectrum $Nd_2Fe_{14}Mn_3$, the obtained fit had a broad doublet sign of a paramagnetic state that takes place for this compound at 300 K. The broaden doublet is due to structural disorder, indicating that there are different Fe positions and therefore different contributions to magnetic moment, which Mössbauer spectroscopy reach is unable to resolve.

4. Conclusions

The substitution of Mn by Fe brings as consequence a little increase of T_c for small x values with a maximum in $x = 0.2$ but a diminution in temperature is observed at larger concentrations, unlike the $Nd_2Fe_{17-x}Ga_x$compound where the temperature increases up to $x = 3$. The difference between these two behaviors can be explained because the Ga replaces Fe sites by modifying the Fe – Fe interatomic distances, while for the Mn case, the initial increase in Curie temperature is due to the lattice expansion. However, the increase in the concentration of Mn induces antiferromagnetic interactions which reduce the magnetization at the Fe site with the highest number of Fe atom nearest neighbors.

In $Nd_2Fe_{14}Ga_3$Mössbauer spectrum at room temperature the presence of sites which responds to the α-Fe hyperfine field was observed, which contributes to the magnetization of the compound. Also a paramagnetic behavior in $Nd_2Fe_{14}Mn_3$ was observed.

In addition, in Mössbauer spectra of the $Nd_2Fe_{17-x}Mn_x$ (x = 0.2, 0.4) and $Nd_2Fe_{14}Ga_3$solid solutions, the presence of sites which correspond to the α-Fe hyperfine field was observed. However, for $Nd_2Fe_{17-x}Mn_x$compounds these sites present IS and QS values which are far from those of pure Fe values, suggesting the presence of Fe clusters with impurities of Nd and Mn. This clusters increases the global magnetization of the compound that decrease when increase Mn concentration.

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