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# Magnetic behavior of $Nd_2Fe_{17x}Mx$ (M=Mn, Ga): A comparative study

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Samples of $Nd_2Fe_{17-x}M_x$, with M = Mn and Ga, were prepared by arc melting and homogenized by annealing at T = 1273 K. Afterwards, specific heat, impedance, X-ray diffraction, Mossbauer spectroscopy, and thermogravimetric measurements were carried out. Results indicate that temperature dependence on impedance changes at transition temperature. Specific heat measurements show an anomaly at transition temperature and this is compared with data reported for $Y_2Fe_{17}$ and $Pr_2Fe_{17}$. Specific heat jump $\Delta C_p$ for $Nd_2Fe_{17-x}Mn_x$ as a function of $x$ at transition temperature was obtained from experimental data; this exhibits a decreasing behavior but different from that predicted by the expression derived from the molecular field theory. This disagreement could be attributed to competition between enlarged Fe sublattice and reduction of magnetic moment when Mn is substituted by Fe at preferential sites. On the other hand, substitution with Ga contributes to increasing transition temperature up to T = 552 K for $x$ =3, as a consequence of enlarged Fe-Fe ion distance producing an increase of ferromagnetic interactions.

*Keywords:* Fe and its alloys; specific heat; magnetic; thermoelectric and thermomagnetic effects.

Se prepararon muestras de $Nd_2Fe_{17-x}M_x$, con M = Mn y Ga, por fusión en horno de arco y se homogenizaron con tratamiento térmico a 1273 K. Posteriormente, fueron llevadas a cabo medidas de calor específico, impedancia, difracción de rayos X, espectroscopía Mössbauer y termogravimetría magnética. Los resultados indican que la Impedancia en función de la temperatura cambia a la temperatura de transición. Las medidas de calor específico presentan una anomalía a la temperatura de transición y esta se compara con los datos reportados para los compuestos $Y_2Fe_{17}$ y $Pr_2Fe_{17}$. El salto en el calor específico $\Delta C_p$ para $Nd_2Fe_{17-x}Mn_x$ en función de $x$ en la temperatura de transición obtenido de los datos experimentales, presenta un comportamiento decreciente en forma diferente a lo predicho por una expresión derivada de la teoría de campo molecular. Este desacuerdo podría ser atribuido a la competición entre el ensanchamiento de la subred de Fe y reducción del momento magnético cuando se sustituye el Mn por el Fe en sitios preferenciales. Por otro lado, la sustitución con Ga contribuye a incrementar la temperatura de transición hasta T = 552 K para $x$ =3, como consecuencia del aumento de la distancia Fe-Fe entre los iones que produce un aumento de las interacciones ferromagnéticas.

*Descriptores:* Fe y sus aleaciones; calor específico; efectos termoeléctricos y termomagnéticos.

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## 1. Introduction

Within the two recent decades, $R_2Fe_{17}$ has attracted research attention because of the potential uses of these materials as permanent magnets [1,2] or in magnetic refrigerators [3,4]; however, low transition temperature and magnetic anisotropy might be improved in these materials to increase the practical uses of these compounds. For this purpose, substitution of Fe for Mn [5], Ga [6], Al [7], Si [8], and Be [9] can be used to modify interactions between M-M ions that result in changes of magnetic temperature transition and/or magnetic behavior. One of the methods for studying the effect of substituting M ions on Fe sites is through transport properties, which contribute to clarity about modification of $T_c$ and saturation magnetization ($M_s$) in these compounds. $Nd_2Fe_{17}$ has a hexagonal structure with $Th_2Zn_{17}$-type and ferromagnetic behavior with no collinear Nd and Fe magnetic moments. This complex magnetic structure can be changed by Fe preferential substitution of Fe ions where 6c are the most probable sites of occupation for substitution ions, and this site corresponds to a dumbbell pair site in the $Th_2Zn_{17}$ structure [10]. The magneto-volume effect observed in these compounds can be explained because the 6c site has the largest Wigner-Seitz cell (WSC). The substitution of the $Fe^{+3}$ ion for $Mn^{+2}$ can induce additional modifications to this compound, taking into account that the ionic radii of Mn is greater than for Fe, an increase of ferromagnetic interactions by expansion of lattice parameter; however, Mn decreases magnetic moments of the 3d sublattice in $R_2Fe_{17-x}Mn_x$ as determined by neutron diffraction measurements [11]. For Ga, transition temperature increases with Ga content growth to $x$ = 3 and then decreases; the rise of $T_c$ can be explained by increasing ferromagnetic interactions given that Ga substitution enlarges separations between Fe ions, further increasing Ga content can decrease saturation magnetization and $T_c$ by diluting magnetic effect.

Several studies on the magnetic behavior of these compounds has been reported, but an additional analysis of non-monotonic $T_c$ behavior when substitution with Mn is done and the relation between substitution of Fe and transport properties, especially specific heat, might be conducted to evaluate the role of Fe substitution on thermal properties in these materials. Detailed knowledge of these properties, especially their thermal properties is a motivation of the present work.

## 2. Experimental procedure

Polycrystalline samples of $Nd_2Fe_{17-x}M_x$ with M = Mn and Ga were prepared by arc melting in high-purity argon atmosphere. Nd, Fe, Mn, and Ga were used at 99.9% purity. A 3% excess of Mn and Ga was added to compensate for weight loss during melting. Ingots were melted four times to ensure homogeneity; weight loss after melting was $< 6\%$. After melting, they were wrapped with Ta foil and sealed in a silica vacuum tube and annealed at 1273 K during 14 hours and then quenched to room temperature. Samples were taken for specific heat, impedance spectroscopy, XRD, and magnetic thermogravimetric measurements. Impedance spectroscopy was conducted in a Solartron 1260; for thermal measurements DSC, MDSC, and MTG we used a TA 2560 and TA 2050, respectively. Mössbauer spectroscopy measurements were conducted in standard transmission geometry on a conventional spectrometer at room temperature.

## 3. Results and discussion

Impedance spectroscopy measurements were performed in the range near to transition temperature, no magnetic field was applied. The frequency of measurements was from 10 Hz to $10^6$ MHz and amplitude of 5 mV. This frequency is expressed by. Impedance measurements results for $Nd_2Fe_{16.6}Mn_{0.4}$ are presented in the Nyquist diagram (Fig. 1), which shows a decrease of the Z" maximum value from T = 328 K to T = 343; this fact can be explained from L'= (-jG/w)Z' (L' is complex impedance and G is a geometric factor), regarding that, the temperature transition for this compound is $T_c$= 337 K. Similar results were obtained for other $Nd_2Fe_{17-x}Mn_x$ compounds near Curie phase transition. For $Nd_2Fe_{16.6}Ga_{0.4}$, comparable behavior is observed for impedance measurements close to transition temperature.

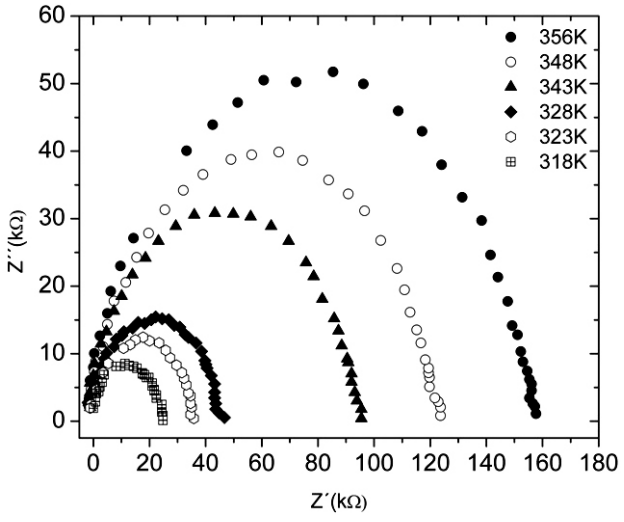


FIGURE 1. Nyquist diagram from impedance measurements for $Nd_2Fe_{16.6}Mn_{0.4}$.

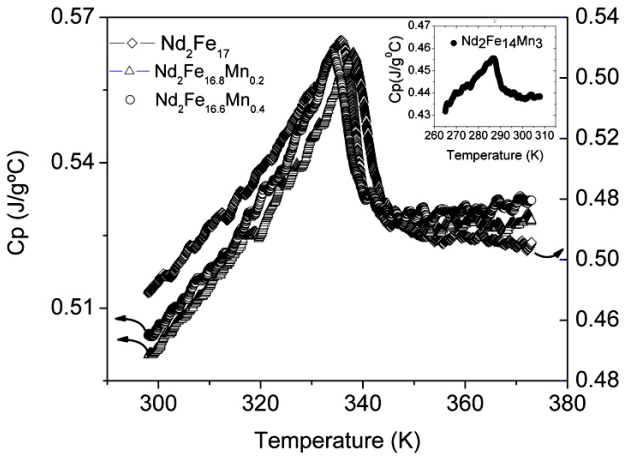


FIGURE 2. Specific heat measurements as functions of temperature near $T_c$ for $Nd_2Fe_{17-x}Mn_x$ obtained from MDSC. Left and right scales associate with respective curves as indicated by the arrows.

On the other hand, specific heat measurements at zero magnetic field were conducted in these samples near to transition temperature. From these measurements, an anomaly at $T_c$ is evident as a jump of specific heat when the sample magnetic behavior shifts from ferromagnetic to paramagnetic. Previous calibration temperature and specific heat measurements were carried out to obtain accurate values of specific heat in these compounds.

Specific heat measurements for $Nd_2Fe_{17-x}Mn_x$ are displayed in Fig. 2. These measurements were conducted in samples near to transition temperature by using the MDSC at zero magnetic field. In the insert, $Nd_2Fe_{14}Mn_3$ shows a jump of specific heat. An analysis of data for specific heat requires measurements in the whole range of temperature that takes into account contributions from the electronic, phonon and magnetic part; however, we have tried to gather technical data and information from literature about another compound like $Pr_2Fe_{17}$ that is very close to $Nd_2Fe_{17}$. To ensure accurate data analysis, technical information was collected; in this case, sapphire specific heat data provided by TA instruments has been used to calibrate DSC [12]. Also, electronic contribution to specific heat at low temperatures for Pr was used to obtain $\gamma$ and $\beta$ parameters from data experimentally reported by Mandal, *et al*., [4]. This approach can be used to obtain an approximation to our data in a broader temperature range than corresponding to our measurements.

Debye temperature in the $Nd_2Fe_{17}$ compound was taken from reported experimental data [13]. Analysis of specific heat behavior agrees with the expected behavior for second-order phase transition; there is no discontinuity in entropy but a jump of $C_p$ ($\Delta C_p$) is present. It is worth noting that for $R_2Fe_{17}$ compounds this behavior is present as Pr and Y compounds and it is expected that the same behavior will be present in the solid-state $Nd_2Fe17_{-x}Mn_x$ solutions, because the substitution of Mn at preferential sites of Fe results in competitive effects that reduce ferromagnetic interactions [10]. This specific-heat anomaly with a broad temperature range can be suitable for magnetocaloric effect materi-

als where there is a desirable enhancement of these features for such materials because the refrigerant capacity is related to the product between $\Delta S_m$ and $\Delta T$ [14]. To obtain transition temperature, we used as criteria the maximum value obtained from derivate temperature dependence of specific heat ($dC_p/dT$). At this temperature, a jump of specific heat is observed. We measured $\Delta C_p$ from experimental data, and compared it with calculated values by using the expression derived from molecular field theory, as given below (Bushow, *et al.*, [15]).

$$\Delta C_p = \frac{5J\left(J+1\right)Nk}{J^2+\left(J+1\right)^2} \tag{1}$$

In this instance, we used a contribution of J from the expression:

$$J = 2J_{Nd} + (17-x)J_{Fe} + xJ_{Mn} \tag{2}$$

Where we used $J_{Nd}$= 9/2, $J_{Fe}$= 4 and $J_{Mn}$= 5/2 with these values to plot $\Delta C_p$ vs concentration (x) and it can be observed from Fig. 3 that both experimental and calculated $\Delta C_p$ values decrease as a function of x, but in different ways. Given that experimental values of $\Delta C_p$ can be affected by short-range interactions taking place above $T_c$, we extrapolated our experimental data below and above $T_c$ by using specific heat of the reported $Pr_2Fe_{17}$ compound and calibration data of DSC for sapphire to extract more exact values of $\Delta C_p$. The disagreement between experimental and calculated values of $\Delta C_p$ can be associated to preferential substitution of Mn ions at the Fe sublattice, given that Mn contributes to expanding the Fe sublattice; thus, increasing ferromagnetic interactions while decreasing the magnetic moment. Another fact is some kind of disorder when substitution of Mn increases at the Fe site, as detected by Mössbauer Spectroscopy [16].

We point out that Curie temperature as a function of concentration increases up to $x$ = 0.2 and then decreases to further x values in $Nd_2Fe_{17-x}Mn_x$ compounds; this fact is not

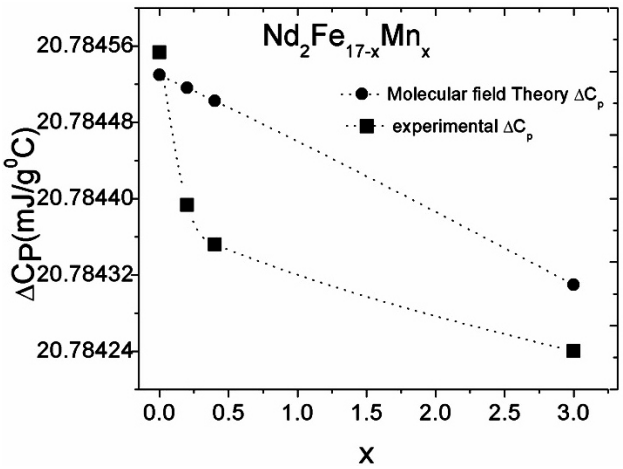


FIGURE 3. $\Delta C_p$ vs x for $Nd_2Fe_{17-x}Mn_x$ from experimental data and for an expression derived from molecular field theory, dotted line is a visual guide.

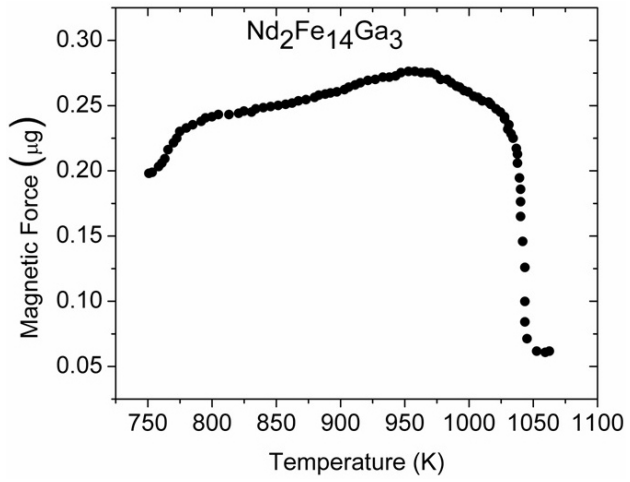


FIGURE 4. Temperature dependence of magnetic force for $Nd_2Fe_{14}Mn_3$ where an important decreased behavior is observed at 1042 K, associated with ferromagnetic phase transition of the $\alpha$-Fe phase.

reflected in Fig. 3 where the initial increase of the transition temperature results from the rise of ferromagnetic interaction by expansion of the Fe-Fe distance. But, $T_c$ decreased with further increasing of x faster than increasing the Fe-Fe distance. Competition between the separation of Fe ions and increased antiferromagnetic interactions in $Nd_2Fe_{17-x}Mn_x$, which reduces saturation magnetization at the Fe sublattice with increasing Mn content, can explain this fact. On the other hand, results for $Nd_2Fe_{17-x}Ga_x$, compounds show that transition temperature increases to $T_c$= 540 K for $x$ = 3. In this case, substitution of Ga enhances ferromagnetic interactions up to $x$ = 3. Specific heat for $Nd_2Fe_{17-x}Ga_x$shows a similar behavior as $Nd_2Fe_{17-x}Mn_x$ compounds near transition temperature, with an anomaly at this temperature and jump $\Delta C_p$ that decreases with $x$, but there is insufficient experimental data for these compounds that allow formulating any conclusion about this behavior.

Additionally, via Mössbauer spectroscopy and Magnetic Termogravimetry measurements, we found a magnetic $\alpha$-Fe phase for $Nd_2Fe_{14}Ga_3$. This phase was detected through measurements of hyperfine field isomer shift values that provide evidence of the presence of an undesirable $\alpha$-Fe phase. Magnetic force measurements allowed identifying a transition temperature through further decrease of magnetic force as a function of temperature that occurs at T = 1042 K, as noted in Fig. 4.

## 4. Conclusions

We prepared $Nd_2Fe_{17-x}M_x$ compounds with M = Mn and Ga to examine the influence of substituting these elements on $Th_2Ni_{17}$-type compounds. Substitution with Ga increases transition temperature up to T = 540 K with $x$ =3, but an undesirable $\alpha$-Fe phase is present in this compound. Substitution with Mn produces an initial increase of $T_c$ up to $x$ =0.2 and then transition temperature decreases monotonically to

$x = 3$. Impedance spectroscopy measurements show a change of behavior at transition temperature; more detailed measurements, including samples under magnetic field, might be carried out, but they are beyond the reach of the present work. The specific heat of $Nd_2Fe_{17-x}Mn_x$ shows an anomaly at transition temperature and there is a second-order phase transition signal. Calculation of the jump of specific heat at transition temperature by using the expression derived from the molecular field theory as a function of $x$ has a different behavior than the experimental data. Competition effects associated with the substitution of Mn at preferential sites of Fe and disorder in the Fe sublattice when Mn substituted Fe sites can explain this fact [16].

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