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Influence of Fe-substitution on structural, magnetic and magnetocaloric properties of $Nd_2Fe_{17-x}Co_x$ solid solutions

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ABSTRACT

$Nd_2Fe_{17-x}Co_x$ ($x = 0, 1, 2, 3, 4$) intermetallic compounds, obtained under arc-melting conditions, have been investigated by means of X-ray diffraction analysis (XRD), Mössbauer spectrometry and magnetic measurements. The Rietveld refinement revealed that the sample is a pure compound with rhombohedral Th_2Zn_{17}-type structure ($R\bar{3}\,m$ space group) with the following lattice parameters: $a = 8.5792$ (2) Å, $c = 12.4615$ (2) Å. Using Mössbauer spectrometry analysis coupled with structural consideration we have unambiguously determined the cobalt atoms preferred inequivalent crystallographic site. Nd_2Fe_{17} show an increase of 3.5 T in their weighted average hyperfine fields upon cobalt substitution. Whatever the cobalt content, the hyperfine field of these compounds follow this sequence $H_{hf}\{6c\} > H_{hf}\{9d\} > H_{hf}\{18f\} > H_{hf}\{18\,h\}$. The magnetic measurements showed that the Curie temperature increases with the Co content. The magnetic entropy change (ΔS_M) was estimated from isothermal magnetization curves and it increases from 3.35 J/Kg K for $x = 0$ to 5.83 J/Kg K for $x = 2$ at $\mu_0 H = 1.6$ T. The relative cooling power (RCP) is in the range of 11.6 J/kg ($x = 0$) and 16 J/kg ($x = 2$).

1. Introduction

A wide family of magnetic intermetallic compounds arises from the alloy of R (rare earth) and T (transition metal) [1–7]. Localized magnetism of R sublattice combined with an itinerant of T sublattice makes these magnetic intermetallics very attractive for both fundamental and industrial applications.

R-Fe intermetallic compounds display a great variety of crystalline structures and different magnetic behaviors depending on the stoichiometry and the nature of the R atom [8,9]. The intrinsic properties of the R-Fe intermetallics can be understood in terms of exchange interaction and magnetocrystalline anisotropy. The exchange interaction take place between all unpaired R-4*f* and Fe-3*d* electrons. This interaction takes place through the hybridization of the transition metal 3*d* states with the 5*d* ones of the rare-earth [10]. In R-Fe compounds it is generally accepted there are three types of interactions, namely, the R-R interaction between the magnetic moments within the R sublattice, the Fe-Fe interaction between magnetic moments of the Fe sublattice and the R-Fe intersublattice interaction [11,8,12,9,13–16,10].

R_2Fe_{17} intermetallic compounds are considered very attractive systems for studying competing $3d-4f$ magnetic interactions [8]. Recently, requirement for high temperature applications of the permanent magnets have led to extensive research on the rare earth-cobalt rich compounds for higher Curie temperature and improved magnetocrystalline anisotropy [17,18]. It is to note that, depending on the nature of the R atom used, R_2Fe_{17} can be obtained as a rhombohedral $R\bar{3}\,m$ Th_2Zn_{17} type structure or as an hexagonal $P6_3/mmm$ Th_2Ni_{17} type structure, depending on whether it is a light R atom or a heavier R atom respectively [8].

R_2Fe_{17} compounds have low Curie temperature (T_C) values in comparison with other R-Fe intermetallics of similarly high Fe concentration like $R_2Fe_{14}B$ [9,19–23], $RFe_{11}Ti$ [9,14,24–26,16,27,28]. In order to increase the total anisotropy and T_C in these compounds, different approaches have been studied. The rare-earth sublattice anisotropy can be increased by a convenient choice of rare-earth or by reducing the iron sublattice planar anisotropy by substituting a nonmagnetic element for iron [29,8,30–32,9,33,34]. The short dumbbell iron-6*c*-iron-6*c* distance in these compounds is responsible for their low Curie temperatures, and the increase in this bond distance enhances T_C [35,36].

Lately, iron rich R_2Fe_{17} compounds have been studied for their magnetocaloric properties [37–39]. Since the discovery of the giant

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magnetocaloric effect in $Gd_5(Ge,Si)_4$ [40–43], several intermetallic alloys have been studied, among which R-T compounds. This effect portrays the heating and cooling of a magnetic material when undergoing a magnetic field variation. As a direct application, this can be used in new type of refrigerators, heat exchangers or heat pumps. R_2Fe_{17} compounds are especially interesting due to their lower cost of the main component (Fe), and some of them give similar MCE and relative cooling power properties as those of Gd-based materials [37,38,44].

W. B. Yelon et al. have reported the site distribution of some nontransition-metal substituents [45–47,33,48] in the substituted $Nd_2Fe_{17-x}T_x$ alloys (T=Cu, Zr, Nb, Ti, V). Nevertheless, little is known about the site distributions for cobalt.

Recently, we have investigated the isothermal section at 800 °C of the Nd-Fe-Co ternary system, we have found that the solid solubility range of Co in Nd_2Fe_{17} form discontinuous series of two ranges between about 0 – 30.14 at% Co, and 51.9 – 100 at% Co [49].

The goal here was to study the Co effect on structural, Mössbauer spectrometry and magnetic properties of $Nd_2Fe_{17-x}Co_x$. In our case, the Fe and Co structure factors are very similar, which makes difficult to localize the Co atoms in the structure using the X-ray powder diffraction. Mössbauer spectrometry is however a particularly well suited tool for the NdFeCo systems. As will be shown in this paper, Mössbauer spectrometry, which probes on a microscopic basis the iron atoms on the four inequivalent crystallographic sites, is helpful in understanding the effect of the Co substitution.

Finally, we have studied the low field magnetic entropy changes in Nd_2Fe_{17} compounds and we have demonstrated the magnetocaloric effect enhancement due to Co substitution, observed for the first time for intermetallic compounds.

2. Material preparation and experimental techniques

As-cast ingots, with $Nd_2Fe_{17-x}Co_x$ nominal composition, were prepared from high purity elements Nd 99.98%, Fe 99.99%, Co 99.99% by arc-melting technique. The samples were turned over and re-melted four times to ensure adequate homogeneity. The ingots obtained after melting were broken under an inert argon atmosphere in a glove box [50].

A high-purity, argon-filled glove box with an O_2 and H_2O rate around 1 ppm was used for all powder handling. The as-cast ingots were wrapped in tantalum foil and sealed in silica tubes under a vacuum of 5×10^{-7} Torr, then annealed at 800 °C for one week in order to reach a good homogenization.

The crystal structure was deduced from X-ray-diffraction (XRD) patterns, registered on a Bruker D8 diffractometer, at room temperature, with automatic divergence slit (Cu Kα radiation $\lambda = 1.54178$ Å). The data were collected by 0.015° step width for 13.5 s over a 2θ range from 20° to 80°. The X-ray patterns were refined using the FULLPROF program based on the Rietveld method. The peak-shape function was chosen as Thompson-Cox-Hastings pseudo-Voigt type [51,21,52]. The background was chosen by interpolation between selected points in regions devoid of Bragg reflections. As a measure of the quality of refinement, two agreement factors (R_B and χ^2) from the program output were used:

$$R_B = \frac{\sum_K |I_K(o) - I_K(c)|}{\sum_K I_K(o)} \quad \text{and} \quad \chi^2 = \frac{\sum_i w_i|y_i(o) - y_i(c)|^2}{N - P + C}$$

where $I_K(o)$ is the observed Bragg intensity and $I_K(c)$ is the calculated one. $y_i(o)$ is the intensity observed at the i^{th} step in the step scanned powder diffraction pattern, $y_i(c)$ is that calculated, and w_i is the weight of the observation. N is the total number of points used in the refinement. P the number of refined parameters, and C the number of strict constraint function.

In the final run the following parameters were refined: U, V, W, background points, scale factor, unit cell parameters, positional parameters, isotropic thermal factors and preferred orientation parameters.

The magnetic measurements were carried out using a DSM-8 MANICS differential sample Magneto-Susceptometer, working on the same principle as a Faraday balance. The magnetic transition temperature in studied systems were determined with $M(T)$ measurements carried out in an applied field of 0.12 Tesla and a heating rate of 5 K/min.

In order to carry out magnetic measurements under high temperature conditions, powder samples were sealed in vacuum quartz ampules to protect them against oxidation or any decomposition.

The ^{57}Fe Mössbauer spectra were obtained at room temperature on a Wissel constant-acceleration spectrometer. The γ-radiation is emitted from a source containing the radioactive parent isotope, ^{57}Co, which decays to the excited state of the ^{57}Fe Mössbauer isotope. This excited state decays by recoil-free emission of the Mössbauer γ-radiation with an energy of 14.4 keV or 2.304×10^{-15} J. The transmitted intensity of this radiation through an absorber containing ^{57}Fe atoms in their ground state, is measured as a function of the γ-ray energy, which is varied by Doppler shifting the source relative to the absorber. This explains why the energy scale is given in mm/s and why energies are measured in mm/s by Mössbauer spectrometry. The vertical scale of a Mössbauer spectrum is given in percent transmission or percent absorption and an important quantity for the spectroscopist is the absorption area of the spectrum. This area is a measure of the recoil-free fraction of the absorber, which is the fraction of nuclei undergoing recoil-free absorption.

The Wissel constant-acceleration spectrometer utilized a 25 mCi rhodium matrix cobalt-57 source. The spectrometer was calibrated at room temperature with α-iron foil, the calibration gives a line-width of 0.25 mm/s for α-Fe. The Mössbauer absorbers, which were 25 mg/cm^2 thick, were prepared from powdered samples. The spectra were fitted according to the procedure discussed later with estimated errors of ±0.1 T for hyperfine fields H_{HF} and ±0.005 mm/s for isomer shifts δ and quadrupole shifts $2\ \varepsilon$.

3. Results and discussion

3.1. Structure analysis

$Nd_2Fe_{17-x}Co_x$ compounds crystallize in the rhombohedral Th_2Zn_{17}-type structure (space group $R\bar{3}\,m$), in which the iron atoms occupy four inequivalent $6c$, $9d$, $18f$, and $18\,h$ crystallographic sites (Fig. 1) and a unique $6c$ site is occupied by the neodymium. This $6c$ site, the so called "dumbbell site" plays an important role on the magnetic properties of the Nd_2Fe_{17} compound. It is interesting to note that the arrangement of atoms around the transition metal $6c$ sites is quite similar to that for the RCo_5 system.

This structure is derived from a hexagonal $CaCu_5$-type structure by

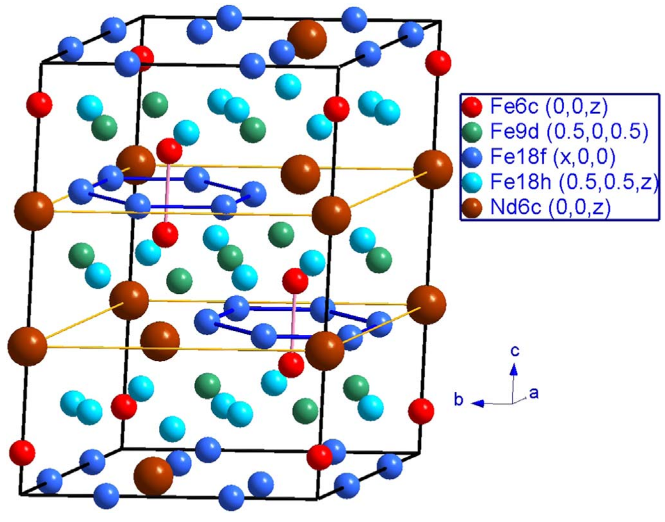

Fig. 1. Crystal structure of the rhombohedral $R\bar{3}\,m$ Nd_2Fe_{17} compound.