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Magnetic and electronic properties of nanocrystalline $Dy_xLa_{1-x}Ni_5$ compounds obtained by high energy ball milling

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$Dy_XLa_{1-X}Ni_5$ compounds have been obtained by mechanical milling in a high-energy planetary mill and subsequent annealing under vacuum for different times. Magnetic measurements were performed in the temperature range 4.2–300 K and fields up to 5 T. There is a transition from spin fluctuation behaviour, characteristic for $LaNi_5$, to a ferrimagnetic type ordering for $x \geq 0.2$. Band structure calculations were also performed The differences between magnetic moments at 2c and 3g sites, obtained from band structure calculations, were correlated with their local environments The influence of the milling and annealing conditions on the structural and magnetic properties of $Dy_XLa_{1-X}Ni_5$ compounds has been investigated. The magnetocaloric effect was also studied.

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1. Introduction

The transition metal atoms (M) in rare-earth (R) or yttrium compounds show a wide variety of magnetic behaviors. As function of crystal structure and composition, these cover the situations in which A atoms show a well defined magnetism or are in nonmagnetic state, crossing the region of onset or collapse of magnetism [1]. The transition from nonmagnetic to magnetic state was analyzed mainly in cobalt compounds, by using the molecular field approximation. For this purpose, the exchange field acting on cobalt was computed by using the phenomenological constants describing the exchange interactions between and inside the magnetic sublattices. It was suggested that an induced Co moment will occurs above a critical field of the order of 70 T. Then, the cobalt moments vary linearly with exchange field and finally saturate [2]. The analysis of magnetic behavior of some R-Co and R-Co-B systems confirmed the above model [3-5].

The RNi_5 based compounds, where R is a rare-earth or yttrium were intensively studied in correlation with their use as hydrogen storage materials [1]. The RNi_5 compounds crystallize in a hexagonal structure of $CaCu_5$-type, having P6/mmm space group. In this structure the R atoms occupy 1a-type site, while nickel ones are distributed on 2c and 3g positions. The analysis of the magnetic properties of RNi_5 end series compounds evidenced interesting properties. The Curie temperatures, T_c, are very low, the maximum value, T_c = 35 K, being reported for $GdNi_5$. In earlier studies was suggested that nickel is non-magnetic in RNi_5-series. This fact was correlated with the paramagnetic behavior of $LaNi_5$ and YNi_5 compounds. Later on, analyzing the magnetic properties of $(Gd_xY_{1-x})Ni_5$ [6] and $(Gd_xLa_{1-x})Ni_5$ [7] pseudobinary compounds, has been shown that the mean magnetic nickel moment, at 1.7 K, in $GdNi_5$ is of ≅ 0.17 μ_B/atom, antiparallely oriented to gadolinium moment. The nickel saturation moments decrease when substituting Gd by La or Y and are nil in $LaNi_5$ and YNi_5. In the RNi_5 (R=La,Y) [8,9], the magnetic susceptibilities, χ, at $T \leq 10$ K follow a T^2 dependence. Above a characteristic temperature, T^*, the χ^{-1} vs T shows a linear dependence as described by a Curie-Weiss law. The magnetic behavior of these systems was analyzed in the spin fluctuation model [10].

In this paper we analyze comparatively, the crystal structures and magnetic properties of $Dy_xLa_{1-x}Ni_5$ system prepared by high energy ball milling method. In addition to magnetic measurements the magnetocaloric effect was studied too. Band structure calculations were also performed.

2. Experimental

The alloys with the nominal composition of $Dy_XLa_{1-X}Ni_5$ were prepared by high-energy ball milling technique of a mixture of Dy, La and Ni (99.99%). The milling was performed in a Fritsch planetary mill for 2 hours to low energy, to induce god homogeneity, followed by a high energy milling for 5h under high-purity argon atmosphere at room temperature. For milling a grinding bowls speed rotation, 1320 trs/sec, supporting disc rotation, 600trs/sec was used. The ratio of balls weight/powder weight was 5. This technique unlike melt spinning avoids the liquid state and is particularly suitable for volatile elements as encountered in rare earth-based alloys. It follows a good control of stoichiometry with reproducible results. In order to investigate the influence of the heat treatment on the evolution of the structural and magnetic properties, the samples of milled powder were sealed in evacuated silica tubes and heated at 1000°C for different

times.

X-ray diffraction (XRD) was carried out with Cu K_α radiation on a Bruker D8 X Advance diffractometer with the $K_{\alpha 1}$ radiation of copper (λ = 0.15406 nm). The intensities were measured from 2θ = 20° to 100°.

The magnetisation curves were recorded at 4K by the

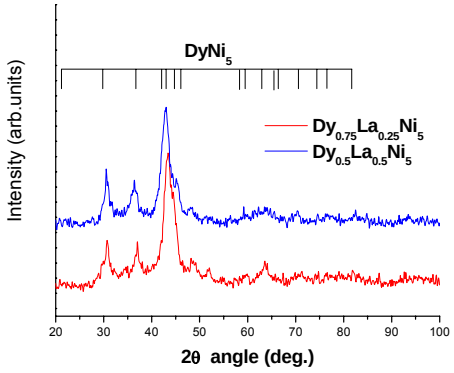

Fig. 1. X-ray diffraction patterns of the $Dy_xLa_{1-x}Ni_5$ (x= 0.25, 0.5) milled for 5 hours.

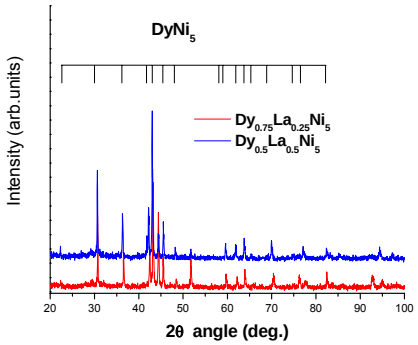

Fig. 2. X-ray diffraction patterns of the $Dy_xLa_{1-x}Ni_5$ sample milled for 5 hours and annealed at 1000 °C for 2 hours.

extraction method in a continuous magnetic field up to 5 T [11]. The saturation magnetizations M_s, were determined from magnetization isotherms, according to approach to saturation law: $M = M_s(1-a/H)+\chi_0 H$. By a is denoted the coefficient of magnetic hardness and χ_0 is a field independent susceptibility. Above the Curie points, the susceptibilities, χ, were determined from their field dependences, according to Honda-Arrott plot [12], $\chi_m=\chi+cM'_sH^{-1}$, by extrapolating the measured values χ_m to $H^{-1}\rightarrow 0$. By c is denoted a presumed magnetic ordered impurity content and M'_s is their saturation magnetization. By this method any possible alteration of magnetic susceptibilities, as result of the presence of magnetic ordered phase, is avoided. Generally, no magnetic ordered phases, above T_c, were observed. Even when exist, these are smaller than 0.1 mol %. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \\ = \frac{1}{\Delta T}\int_0^{H_0}[M(T+\Delta T,H) - M(T,H)]dH \quad (1)$$

where ΔT is the temperature increment between measured magnetization isotherms (ΔT = 3K for our data). The magnetic cooling efficiency was evaluated by considering the magnitude of the magnetic entropy change, ΔS_m and its full-width at half-maximum (δT_{FWHM}). The product of the ΔS_m maximum and the ($\delta T_{FWHM}=T_2-T_1$):

$$RCP(S) = -\Delta S_m(T,H) \times \delta T_{FWHM} \quad (2)$$

is the so-called relative cooling power (*RCP*) based on the magnetic entropy change.

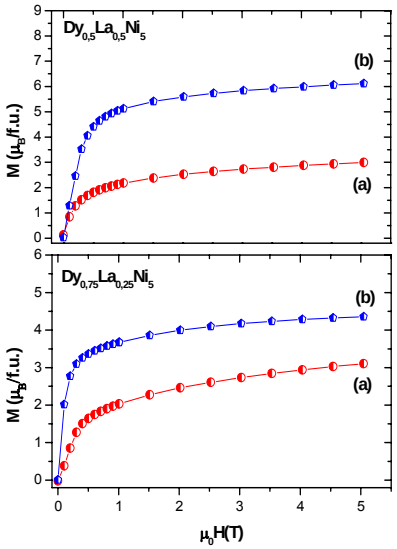

Fig. 3. Magnetization isotherms for $Dy_xLa_{1-x}Ni_5$ compounds mechanical milled (a) and annealed (b).

Band structure calculations were carried out by using the LSDA+U method. The LSDA+U [13] scheme, introduces a simple mean-field Hubbard like term to the LSDA functional. This approach can be viewed as a density functional approach since the U term depends on the occupation number for localized electrons and is determined by the total density. In the actual calculations we have used for the averaged local Coulomb interaction the value U=6 and the exchange parameter J=0.9. A Dy_3Ni_{15} superstructure having three times greater unit cell than that of $DyNi_5$ was assumed. In this cell, the Dy was substituted by one, two or three lanthanum atoms, corresponding to compositions x = 0.67, 0.33 and 0.

3. Results and discussion

XRD patterns of the as milled $Dy_XLa_{1-X}Ni_5$ (x = 0.25, 0.5) are presented in Fig. 1. The Bragg peaks corresponding

to $DyNi_5$ phase are broadened by milling but no additional peaks are observed. As a consequence of the induced internal stresses and decrease of the crystallites size, after milling, the width of the diffraction peaks increases and the high angle peaks become progressively undetectable. The small crystallite sizes and the large microstrains for long milling times given by severe plastic deformation are accompanied by a high degree of structural disorder [14,15].

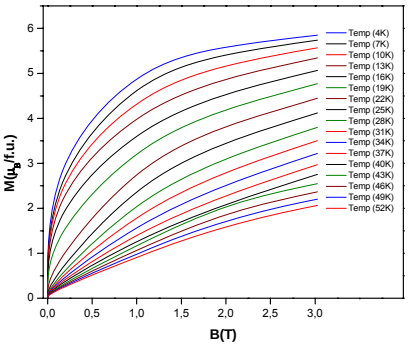

Fig. 3. Magnetization isotherms taken around transition temperature for the compound with x=0.75.

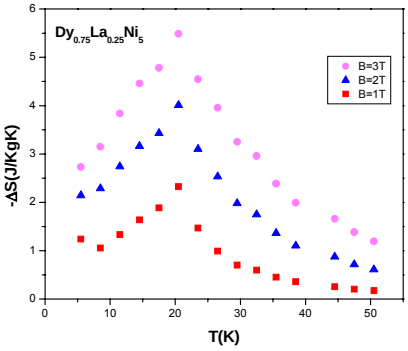

Fig. 4. Magnetic entropy changesaround transition temperature for the compound with x=0.75.

The mean size of the nanocrystallites, calculated from Full-Width-at-Half-Maximum - FWHM of the $DyNi_5$ diffraction peaks according to Scherrer's formula [16] leads to a mean value of about 5 nm after 5 hours milling.

The heat treatment is very efficient in the refinement of the structure (Fig. 2). Progressive developments of the $DyNi_5$ characteristic peaks were observed by annealing. The width of the diffraction peaks decreases in comparison to the corresponding milled sample. The sharper peaks of the X-ray diffraction patterns can be attributed to a decrease in the internal stresses. The mean size of the nanocrystallites $Dy_xLa_{1-x}Ni_5$ (x= 0.25, 0.5) are of about 65-70 nm for 5 hours milling and annealed at the indicated time. A small amount of Ni was observed for the both composition which decrease with the lanthanum concentration.

Some magnetization isotherms before and after annealing are plotted in Fig. 3. There are high differences between the magnetizations, the values for the samples as milled being smaller with around $3\mu_B$ for x=0.75 compared with the values obtained for the annealed sample. This high difference can be explained by the presence of Dy_3Ni and unreacted Ni in the milled sample as was shown by the Rietveld analysis. The total calculated amount of Dy_3Ni is around 10% The total magnetic moment is lower because Dy_3Ni has antiferromagnetic behaviour at low temperatures [17].

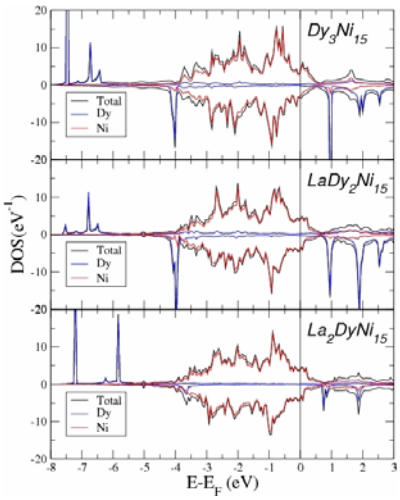

Fig. 5. Dy_3Ni_{15}, Dy_2LaNi_{15} and $DyLa_2Ni_{15}$ densities of states.

The magnetic entropy changes were calculated according with Eq. 1 from magnetization isotherms. As an example in Fig. 4. we present these curves for the sample with x =0.75. Similar behaviour was obtained in all cases. The temperature dependence of the magnetic entropy change for this sample is shown in Fig. 5. A maximum of 5.6 J/(kgK) was obtained in a 3T external magnetic field. In the case of samples with lower Dy content the -ΔS values have smaller values. RCP(S) values between 146 J/kg (in 3T) and 21 J/kg (in 1 T) were determined.

The total densities of states as well as the partial DOS for Ni and Dy projected bands for $Dy_xLa_{1-x}Ni_5$ compounds with x = 1.0; 0.67 and 0.33 are plotted in Fig. 5. A gradual increase of the exchange splitting both at Ni(2c) and Ni(3g) sites was evidenced when increasing dysprosium content. The computed magnetic moments, at various Ni sites, as well as Dy 5d band polarization decrease when increasing La content. In addition, a polarization of La5d band is induced in magnetic ordered compounds. The Dy5d and La5d band polarizations are parallel to Dy4f moments and antiparallel to Ni ones, respectively.

The computed magnetic moments at Ni(3g) sites are higher than those of 2c sites being $0.22\mu_B$(3g) respectively 0.14 μ_B (2c) for x=1; 0.16 μ_B (3g), 0.08 μ_B (2c) for x=0.67 and 0.13 μ_B (3g), 0.06 μ_B (2c) for x=0.33. This behaviour may be attributed to different local environments. The 2c site in $DyNi_5$ has 6Ni(3g) and 3Ni(2c) atoms as well as 3Dy ones, while the 3g sites have 4Ni(2c), 4Ni(3g) and 4Dy as nearest neighbours. The strength of exchange interactions between nickel atoms and dysprosium ones are more important than between nickel atoms. The nickel moments

are essentially induced by the exchange interactions due to presence of Dy. Thus, the exchange splitting of Ni(2c) 3d band is greater than for Ni(3g) sites since of the higher number of Dy nearest neighbours. The La substitution by Dy, leads to the variations of the exchange interactions and consequently to different exchange splitting of Ni3d bands when increasing dysprosium content.

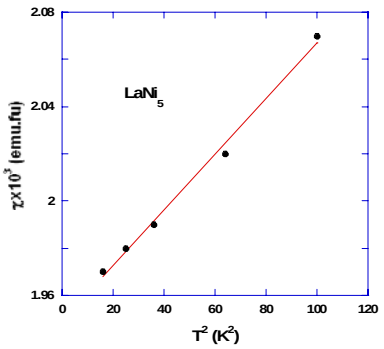

Fig. 6. The T^2 dependence of the susceptibilities at $T \leq 10$ K.

The magnetic susceptibilities for $LaNi_5$, at low temperatures ($T < 10$ K), follow a relation of the form $\chi = \chi_0(1+dT^2)$-see Fig. 6, typical for a Pauli-type paramagnetic system. The d value obtained from band structure calculation agrees well with that experimentally determined. Above $T^* \approx 150$ K, the reciprocal susceptibilities follow a Curie-Weiss-type behaviour with a negative paramagnetic Curie temperature. In case of magnetic rare earth-nickel compounds, as $GdNi_5$ a magnetic moment is induced on nickel at low temperatures. An effective magnetic moment was shown at T>Tc. In addition, the XPS measurements at room temperature show that there are holes in Ni 3d band [18]. Similar behaviour was shown in cobalt exchange enhanced paramagnets as YCo_2 and $LuCo_2$ [19,20]. The magnetic behaviour of nickel in RNi_5-based compounds can be analysed in models which take into account the electron correlation effects in d-band, as spin fluctuation model [10] or dynamical mean field theory [21]. The above models reconcile the dual character of electron, which a particle, requires a real space description and as a wave, a momentum space description. According to the last model, for an itinerant electron system, the time dependence of the correlation function results in a temperature dependence of fluctuating moments. Fluctuating moments and atomic like configurations are large at short time scale. The moments are reduced at larger time scale. In spin fluctuation model [10] the balance between longitudinal and transverse spin fluctuations is considered. This leads to the concept of temperature induced moments, when the frequency of transverse spin fluctuations are higher than of the longitudinal ones.

4. Conclusions

In conclusion in $Dy_xLa_{1-x}Ni_5$, system there is a transition from spin fluctuations behaviour, characteristic for $LaNi_5$, to a ferrimagnetic type ordering for $x \geq 0.2$. The 4f–3d exchange interactions are mediated by R5d band. The Dy5d band polarization is due both to local 4f–5d exchange and 5d–3d and 5d–5d band hybridizations by short range exchange interactions with neighbouring atoms. The mean effective nickel moments decrease when increasing dysprosium. The magnetic behaviour of nickel can be described in the spin fluctuation model. The magnetic entropy change have maximum values around 6 J/(kgK) in a 3T external magnetic field. The relative cooling power have enough high values to could consider this system for technical applications.

Acknowledgments

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