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COMPARATIVE STUDIES OF STRUCTURAL, MAGNETIC AND ELECTRONIC PROPERTIES OF $NdNi_4Al$ AND $NdNi_4B$ COMPOUNDS

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Abstract: We present our results on magnetic and structural studies of the hexagonal rare-earth based $NdNi_4Al$ and $NdNi_4B$ compounds. In spite of different crystallographic structures $NdNi_4Al$ and $NdNi_4B$ compounds exhibit many similarities in their magnetic and transport properties. The ferromagnetic ordering temperature T_C and magnetic moments at 6 T for these compounds are 6 K, 1.52 μ_B/f.u. and 11.7 K, 1.68 μ_B/f.u., respectively. In the case of the $NdNi_4Al$ sample we have performed also neutron diffraction studies, which are not possible for compounds containing natural boron due to the large absorption. Hence, the magnetic order of $NdNi_4Al$ has been established with the magnetic moments ordered in the hexagonal basis plane. Besides, a negligible magnetic contribution of Ni atoms was observed. This condition simplifies the interpretation of the magnetic, transport and electronic properties of RNi_4Al or RNi_4B (R = rare earth or Y) compounds. The photoemission spectra (XPS) of the valence band region at the Fermi level exhibits the dominance of the Ni (3*d*) states (1.5 eV).

1. INTRODUCTION

The RT_4M compounds, where R denotes a rare-earth or Y, T is a transition element like Ni, Fe or Co and M represents Al, B or Cu, are widely investigated both for the possible as well as partly realized applications and due to the appearance of a variety of basic physical phenomena [1-4]. For some members of these systems large values of anisotropy could be observed, properties like a superconductivity, mixed valence and Kondo effect have been also found [5, 6]. The electronic structure, in spite of the intensive theoretical and experimental investigations, is still not fully explained.

The RT_4B compounds crystallize in the hexagonal $CeCo_4B$ structure, which can be derived from RNi_5 by replacing two Ni atoms at the 2*c* sites in every second layer by B atoms. In the $CeCo_4B$ structure Ni atoms occupy two kinds of crystallographic sites, 2*c* and 6*i*, the rare earth element is also located in two sites 1*a*, 1*b* and boron occupies the 2*d* position [7].

The RNi_4Al compounds crystallize in the hexagonal $CaCu_5$-type structure. R occupies the 1*a* site and Ni(1) the 2*c* site, whereas Ni(2) and Al are statistically distributed on the 3*g* position. These materials attract a considerable attention owing to the previous commercial use of the large

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hydrogen absorption of the $LaNi_5$ alloys [8]. Applications in batteries and for hydrogen storage have also been performed [9]. Magnetic, electronic, structural and thermodynamic properties of $TbNi_{5-x}Al_x$ and $LaNi_{5-x}Al_x$ hydrogen systems have already been carefully studied [10, 11]. The case of R = Gd, Dy and Er was also addressed [12-14].

In this paper we compare the properties of the $NdNi_4B$ and $NdNi_4Al$ compounds basing on our neutron diffraction, magnetometry and X-ray photoemission experiments. However, only the RNi_4Al system has been studied using the neutron scattering because unfortunately the natural B is characterized by a large absorption.

2. EXPERIMENTAL

The RNi_4B compounds were prepared by induction melting of the stoichiometric amounts of the constituent elements in a water-cooled boat, under an argon atmosphere.

The room temperature lattice constants are a = 5.0103 Å, c = 4.0601 Å for $NdNi_4Al$ and a = 5.053 Å, c = 6.954 Å for $NdNi_4B$.

Measurements of the d.c. magnetization and the a.c. susceptibility in a magnetic field up to 9 T and temperature down to 4.2 K were carried out on a MagLab2000 instrument.

Diffraction patterns have been collected on the neutron powder diffractometer SV7-a at the FRJ-2 reactor in the Forschungszentrum Jülich, Germany [15]. The neutron wavelength was 1.0957 Å and temperature was varied between 4.2 K and RT. The experiment was performed with external magnetic fields up to 5 T perpendicular to the horizontal diffraction plane. Additionally, time-of-flight technology was employed between 1.8 and 10 K using the diffractometer ROTAX at the spallation source ISIS in Chilton, U.K. [16].

The XPS spectra were obtained with monochromatized Al-K_α radiation at room temperature, using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with the energy resolution of about 0.3 eV. The Fermi level (E_F = 0) was referred to the gold 4*f*-levels binding energy at 84 eV. All emission spectra were measured immediately after breaking the sample in a vacuum of 10^{-10} Torr. The oxidation of the $NdNi_4B$ and $NdNi_4Al$ surface was checked by observing the O(1*s*) spectra before and after each measurement.

3. STRUCTURAL AND MAGNETIC CHARACTERIZATION

Figure 1 shows the unit cells of the $NdNi_4B$ and $NdNi_4Al$ compounds. It is well visible that the difference between the two structures results from the different locations of B and Al atoms. The Al atoms are on the 3*g* positions and are absent on 2*c* sites, which is established owing to the capability of neutrons to distinguish between Ni and Al due to the different nuclear scattering length. Therefore, by the neutron scattering it is confirmed that in the $NdNi_4Al$ compound Nd occupies the 1*a* site (0,0,0) and Ni(1) the 2*c* site (1/3,2/3,0), whereas Ni(2) and Al are statistically distributed on the 3*g* site (1/2,0,1/2).

Figure 2 presents the neutron diffraction pattern of $NdNi_4Al$ recorded at 4.2 K. Full-pattern Rietveld refinements using FullProf [17] have been performed on the 293 K and the 4.2 K data. The refined lattice constants are a = 5.0103(13) Å, c = 4.0601(7) Å at room temperature and a = 4.9955(14) Å and c = 4.0551(7) Å at 4.2 K. The room temperature X-ray diffraction on

$NdNi_4B$ provided a = 5.053 Å and c = 6.954 Å. Both structures are described in the hexagonal space group P6/*mmm*.

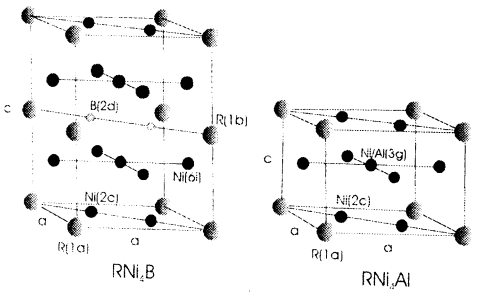

Fig. 1. Unit cell of RNi_4Al and RNi_4B compounds (R = Y or rare earth)

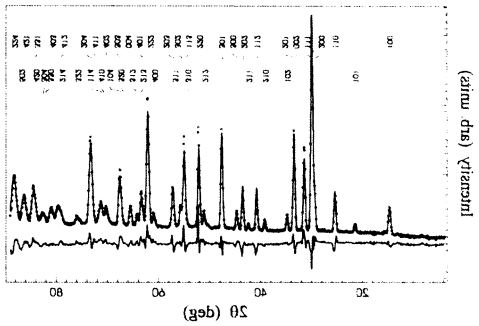

Fig. 2. Neutron diffraction pattern of $NdNi_4Al$ at 4.2 K, experimental data (dots) and refinement (line). The bottom curve represents the difference between measurement and calculation

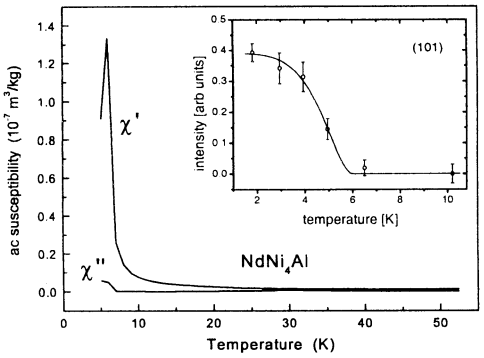

Fig. 3. The real, χ', and the imaginary, χ'', part of the a.c. susceptibility for $NdNi_4Al$. Inset: Temperature dependence of the (101) reflection measured by ROTAX

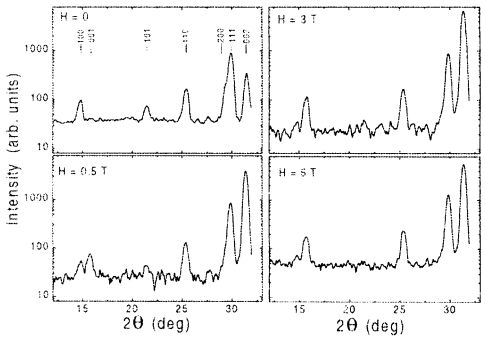

Fig. 4. Low angle part of the neutron diffraction patterns collected at various external magnetic fields indicating the appearance of a long-range ferromagnetic order

The diffraction pattern in Fig. 2 shows neither new magnetic reflections nor noticeable enhancements of intensities on nuclear reflection positions. The long-range ferromagnetic order has been detected using ROTAX. Figure 3 shows the real, χ', and the imaginary, χ'', part of the a.c. susceptibility for $NdNi_4Al$ compound and, as an inset, the temperature dependence of the (101) reflection measured by ROTAX (after the subtraction of the nuclear contribution obtained at RT). Both methods provide the evidence of the para- ferromagnetic phase transition

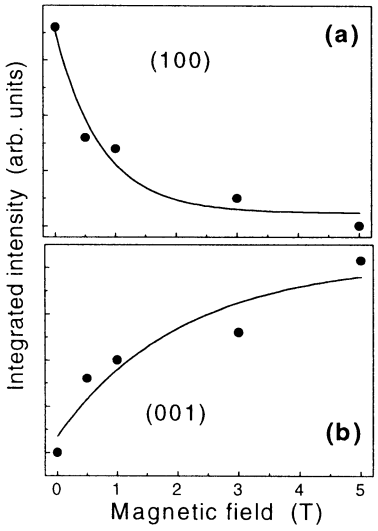

Fig. 5. The field dependence of the (001) and (100) reflection intensities

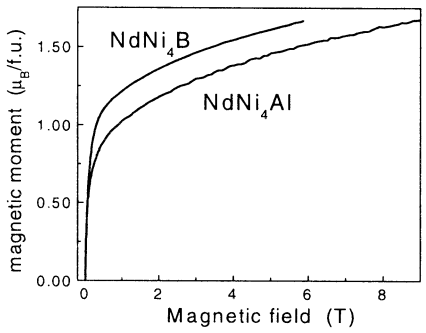

Fig. 6. The magnetization curve of $NdNi_4Al$ and $NdNi_4B$ compounds

at the same temperature of 6 K. In the case of $NdNi_4B$ we have found T_C = 11.7 K from standard magnetic measurements [18]. The neutron diffraction experiments on $NdNi_4Al$, using the diffractometer SV7-a, have been also carried out in external magnetic fields. Figure 4 presents the neutron diffraction patterns at 4.2 K for H in the range from zero to 5 T. Increase of some peaks is visible being the effect of magnetic contributions to the intensities. From the appearance of the (001) and the disappearance of the (100) peak it is evident that the ferromagnetic alignment is perpendicular to the hexagonal axis, i.e., the moments are ordered in the hexagonal basis plane (Fig. 5). The field dependence of the (001) reflection intensities resembles a typical magnetization curve. The field dependence of the $NdNi_4Al$ magnetic moment is shown in Fig. 6 together with the result for $NdNi_4B$ [18]. It is seen that the magnetization curves are similar with a larger moment in the case of $NdNi_4B$. In an external magnetic field H = 6 T the magnetic moment is 1.52 μ_B/f.u. for $NdNi_4Al$ and 1.68 μ_B/f.u. for the $NdNi_4B$ compound. The magnetic moment of $NdNi_4Al$ and $NdNi_4B$ is connected only with the rare earth. This assumption has also been confirmed by the present neutron diffraction studies of $NdNi_4Al$.

4. X-RAY PHOTOEMISSION STUDIES

The valence band of $NdNi_4B$ and $NdNi_4Al$ compounds exhibits the domination of the Ni ($3d$) (E = 1.5 eV) states. Figure 7a shows an example of the valence band for $NdNi_4B$, where a small contribution of the Nd ($4f$) (E = 4.65 eV) peak can be also visible. Peaks at 22.3 eV and 18.7 eV are identified as Nd($5p_{1/2}$) and Nd($5p_{3/2}$). The hybridization between the f-orbitals and the conduction states has been estimated employing the Gunnarsson-Schönhammer model [19].

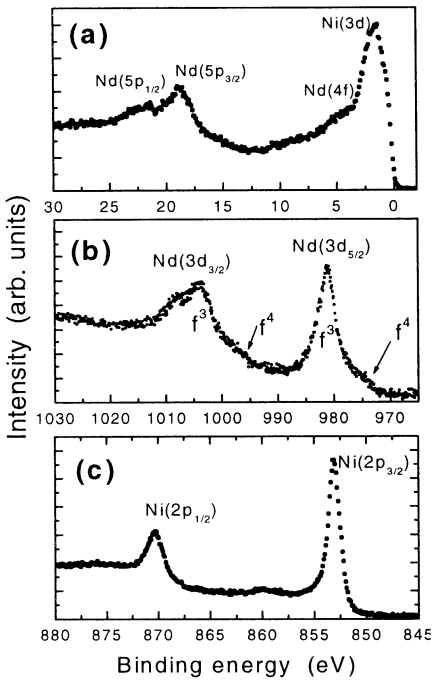

Fig. 7. XPS spectra of $NdNi_4B$ compound (a) valence band, (b) Nd ($3d_{5/2, 3/2}$) doublet and (c) Ni ($2p_{1/2, 3/2}$) peaks

This model bases on the single impurity Anderson Hamiltonian. It was derived for Ce compounds, however can be used for other light rare-earths because the hybridization parameter does not depend on the number of $4f$ electrons. Figure 7b presents the Nd ($3d_{5/2, 3/2}$) doublet using the example of $NdNi_4B$. The value of the $3d$ spin-orbit splitting, E_{LS}, is equal to 22.6 eV. There are additional satellites visible, which enable a rough estimation of the coupling Δ between the f-orbitals and the conduction states [19] basing on the intensity ratio $r = I(f^4)/[I(f^3) + I(f^4)]$, where f^l denotes the XPS final states. Assuming the dependence of the intensity ratio on the Δ parameter like in the case of Ce [19-22] the Δ value is about 23 meV. The values of the parameters are similar to the results for NdAuGe obtained by Szytuła *et al.* [20] ($E_{LS} \approx 22.60$ eV and the coupling energy $\Delta \approx 25$ meV). Figure 7c illustrates the Ni ($2p_{1/2, 3/2}$) peaks in $NdNi_4B$ compound. Between the peaks a satellite is visible typical of Ni metal but of smaller intensity. This may reflect the vanishing Ni moment.

5. CONCLUSIONS

The present magnetic and neutron diffraction studies reveal that:

1) The ferromagnetic ordering temperature T_C and magnetic moments at $H = 6$ T for $NdNi_4Al$ and $NdNi_4B$ compounds are 6 K, 1.52 μ_B/f.u. and 11.7 K, 1.68 μ_B/f.u., respectively. The $NdNi_4Al$ compound in the ferromagnetic phase has the magnetic moments ordered in the hexagonal basis plane. The magnetization curve of $NdNi_4Al$ resembles that of $NdNi_4B$.

2) The valence band is determined mainly by the Ni($3d$) band with small contribution of Nd($4f$) states.

3) The values of the spin-orbit coupling E_{LS} obtained from the R ($3d_{5/2,\ 3/2}$) doublet splitting is equal to 22.6 eV.

4) The hybridization energy, Δ, determined experimentally from the intensity ratio of the Nd ($3d_{5/2}$) peak and its satellite, based on the Gunnarsson-Schönhammer model, is about 23 meV.

5) The Ni atoms provide negligible contribution to the magnetic properties of the studied compounds.

Acknowledgments

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