Coexistence of the magnetically ordered and Haldane states in $(Y_{1-x}Nd_x)_2BaNiO_5$

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Abstract. The magnetic properties of $(Y_{1-x}Nd_x)_2BaNiO_5$ with x = 0.01, 0.02, 0.03, 0.04, and 0.05 are investigated by means of specific heat, magnetic susceptibility, and spectroscopic measurements. We estimate a magnetic contribution of the neodymium subsystem into the magnetic susceptibility and specific heat using temperature dependencies of the splitting of the ground Kramers doublet of the Nd^{3+} ion obtained from spectroscopic experiments. We estimate also the contribution caused by nickel chain breaks and by ferrons. Different scenarios of low-temperature magnetic behavior are discussed.

1 Introduction

In the compounds that contain chains of magnetic ions with the spin S = 1, a disordered ground state with a gap in the spectrum of magnetic excitations (the so-called Haldane gap) is realized [1]. The crystal structure [2] of $(Y_{1-x}Nd_x)_2BaNiO_5$ contains NiO_6 octahedra connected by their apical oxygen ions. The chains directed along the a-axis of the crystal are interconnected through the Nd^{3+}, Y^{3+}, and Ba^{2+} ions. The magnetic system of $(Y_{1-x}Nd_x)_2BaNiO_5$ consists of two kinds of magnetic ions: the Ni^{2+} ions with the S= 1 and Nd^{3+} ions with J=9/2.

Y_2BaNiO_5 is a well-known Haldane system. No long-range magnetic order was detected in this system down to at least 0.1 K [3]. The correlation length was found to be seven lattice constants along the a-axis. Neutron scattering and magnetization studies have revealed a singlet ground state and a gap of about 10 meV in the magnetic excitation spectrum of Y_2BaNiO_5 [4-6].

Total or partial substitution of a magnetic rare-earth (RE) ion for the nonmagnetic yttrium leads to an antiferromagnetic (AFM) ordering. Neutron scattering measurements on $(Y_{1-x}Nd_x)_2BaNiO_5$ with $x \geq 0.25$ have shown that the Néel temperature decreases from 49K (x=1) to 17 K (x=0.25), the magnetic moments of both the Nd and Ni ions are reduced, and the magnetic moments of the Nd^{3+} ions are oriented along the *c* axis, while the magnetic moments of the Ni^{2+} ions lie in the (ac) plane [7]. A combined study of thermodynamic and spectroscopic properties has demonstrated a magnetic ordering of the compound with x=0.15 at 13 K [8]. Inelastic neutron scattering experiments have revealed a coexistence of the Haldane-gap excitations and spin waves in the ordered state and an increase of the Haldane gap with decreasing the temperature below T_N [7, 9].

In this situation, it is not clear how does the Ni subsystem behave in the thermodynamic properties. Another question is whether the magnetic ordering occurs down to the lowest concentration of Nd in the compound or there is a critical concentration below which the system is in a disordered state. In this paper we study specific heat, magnetic susceptibility, and spectroscopic properties of $(Y_{1-x}Nd_x)_2BaNiO_5$ compounds with low concentrations of neodymium.

2 Experimental

Polycrystalline samples of $(Y_{1-x}Nd_x)_2BaNiO_5$ with x = 0.05; 0.04; 0.03; 0.02; 0.01 were synthesized by solid state reactions as described in Ref. [10]. The quality and composition of the samples were tested by x-ray diffraction techniques. The temperature dependencies of the magnetic susceptibility in zero-field-cooled (ZFC) and field-cooled (FC) regimes were measured in the magnetic field of 0.01T at temperatures between 1.8 and 300 K using a MPMS-XL5 SQUID magnetometer (Quantum Design). The temperature dependencies of the specific heat in the temperature range 0.4 ÷ 300K were measured using Heat Capacity options of Physical Property Measurement System (Quantum Design). Optical absorption measurements in the spectral range 10000–15000 cm^{-1} were performed using a Fourier spectrometer BOMEM DA3.002, low temperatures were achived using of a helium-bath cryostat with a possibility to pump helium vapor.

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3 Results

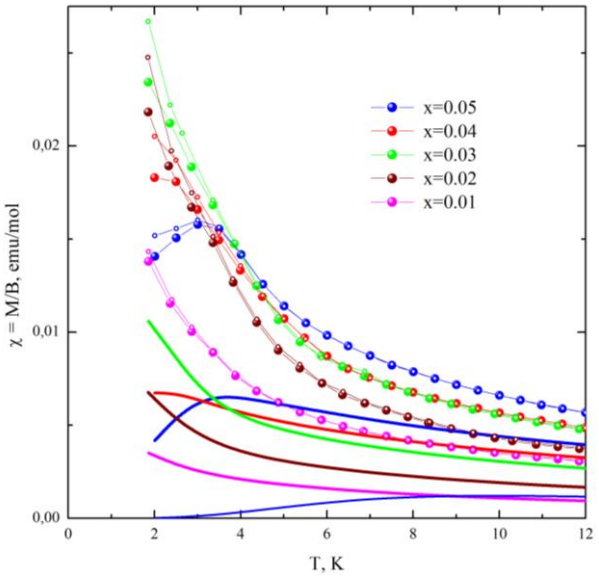

Fig.1. The temperature dependencies of the magnetic susceptibility in a low-temperature range measured in the magnetic field B=0.01 T in ZFC (closed circles) and FC (open circles) regimes for $(Y_{1-x}Nd_x)_2BaNiO_5$. Thick solid lines present the calculated (this work) contribution of the neodimium subsystem. The contribution from chain breaks is represented by thin solid line (only for the compound with x=0.05).

The temperature dependencies of the magnetic susceptibility in the low- and high-temperature ranges are presented in Fig.1 and Fig.2, respectively. The difference in the low-temperature behavior of the magnetic susceptibility measured in ZFC and FC regimes points to a spin-glass state.

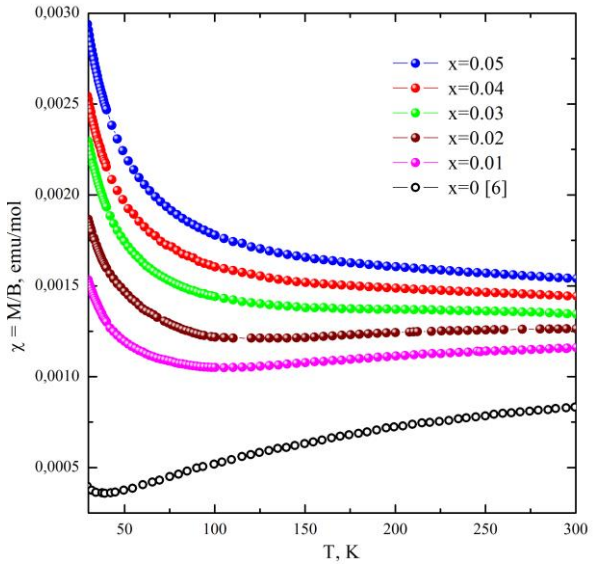

Fig.2. The temperature dependencies of the magnetic susceptibility in a high-temperature range measured in the magnetic field B=0.01 T for $(Y_{1-x}Nd_x)_2BaNiO_5$.

At high temperatures, the behavior of the magnetic susceptibility depends on the Nd concentration in the compound. For compounds with x=0.05, 0.04, and 0.03, the magnetic susceptibility is almost temperature-independent, while at the lowest concentration of Nd, the susceptibility slightly increases with increasing the temperature, similar to the case of the Haldane-gap system Y_2BaNiO_5 [6]. After subtracting the magnetic susceptibility of nickel subsystem taken from the data on Y_2BaNiO_5, we get an estimate for the effective magnetic moment. Its value is close to the free-ion value of Nd in every compound. On these grounds, we argue that the Haldane-gap state of the nickel chains is preserved in the high-temperature range for the studied mixed compounds.

Figure 3 presents the temperature dependencies of the specific heat. A λ-type anomaly observed in the specific heat for compound with x=1, 0.75, 0.50, and 0.25 [11] was not found for compounds with x≤0.05. A maximum observed in specific heat originates mainly from the temperature-driven depopulation of the upper component of the Nd^{3+} ground Kramers doublet (KD) split in an internal magnetic field that appears in the magnetically ordered state.

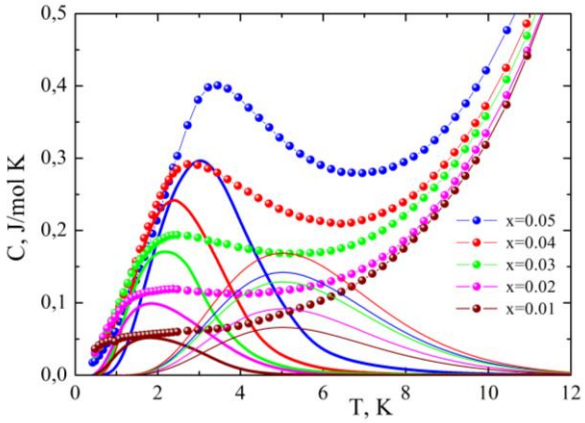

Fig.3. The temperature dependencies of the specific heat in a low-temperature range for $(Y_{1-x}Nd_x)_2BaNiO_5$. The experimental data are represented by circles. Thick solid lines present the contribution of the neodimium subsystem. The contribution from chain breaks is represented by thin solid lines.

In order to estimate the contribution of the Nd system into specific heat and magnetic susceptibility, we used spectroscopic data. For Nd_2BaNiO_5 [12], four spectral lines correspond to four optical transitions between sublevels of the ground and exited KDs split in the internal magnetic field. For mixed compounds, a complex shape of the spectral line is caused by non-equivalent RE centers. Fig. 4a presents the spectral line IA in the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition of Nd^{3+} ion in the compound with x=0.03 measured at different temperatures. At temperatures lower that 4 K this line (as well as other spectral lines) starts to shift to higher energies. We argue that such behavior is connected with the splitting of KDs of the Nd^{3+} ion as it is shown on the scheme of Fig. 4b. Indeed, for Nd_2BaNiO_5 (x=1), the splitting Δ of the ground KD is larger than that Δ_A of the terminal level of the considered optical transition [12] and the same should be valid for any x. In this case, with lowering the temperature, two spectral components

shown by solid lines in Fig. 4 move to the high-frequency side from the line's center, while two other components marked by dash lines symmetrically move to the opposite side and diminish in intensity, due to thermal depopulation of the upper component of the split ground KD. Small line splittings are hidden in the linewidth but the spectral weight shifts to higher frequencies by Δ/2. A similar behavior was observed in the case of $DyMnO_3$ [13]. Thus, spectroscopic data allowed us to find Δ as a function of temperature. With diminishing x, the shift of spectral lines diminishes and starts at lower temperatures

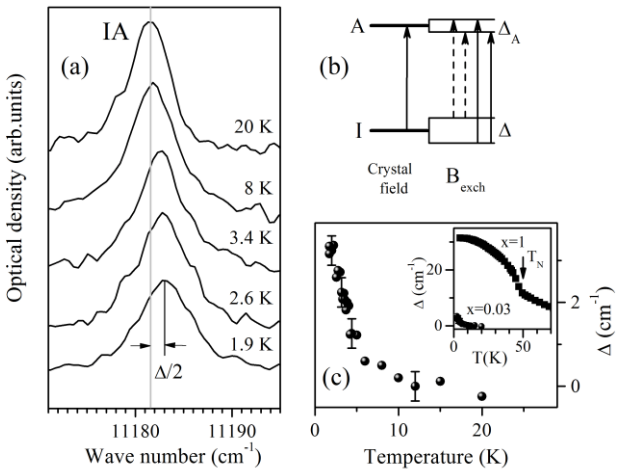

Fig.4. a) The lowest-energy spectral line in the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ intermultiplet transition in Nd^{3+} ion in $(Y_{0.97}Nd_{0.03})_2BaNiO_5$. b) An energy level scheme demonstrating splitting of Kramers doublets in an exchange field. c) Δ(T) function for x=0.03 compound. Inset shows a comparison of Δ(T) functions for the cases of x=1 [12] and x=0.03.

4 Discussion

4.1. Contribution of the neodymium subsystem into specific heat and magnetic susceptibility

The smoothed temperature dependencies of the splitting Δ(T) of the ground KD of the Nd^{3+} ion were used for calculation of the Nd contribution into specific heat and magnetic susceptibility. This contribution of the both neodymium sublattices into specific heat can be written as:

$$C = 2xR\left(\frac{\Delta}{kT}\right)^2 \frac{\exp(\Delta/kT)}{(1+\exp(\Delta/kT))^2}, \qquad (1)$$

where R is the gas constant and k is the Boltzmann constant. The factor $2x$ takes into account the concentration of the neodymium ions in the compound.

In order to calculate a contribution of the neodymium subsystem into magnetic susceptibility, we have to take into account the fact that the neodymium sublattices become nonequivalent in an external magnetic field. The sublattice with the magnetic moment components directed along the external magnetic field is magnetized, and the other sublattice with the opposite magnetic moment directions is demagnetized. An effective magnetic field acting on Nd^{3+} ion results from both an external field B (with components B_α, α = *a, b, c*) and an internal field. The latter one is created, mainly, by the nickel subsystem B_{ex}^{Nd} and is due to the Nd-Ni exchange interaction. We take also the Nd-Nd interaction into account. The components of the effective magnetic field $B_{\text{eff}\,1,2\alpha}$ (α = *a*, *b*, *c*) at the Nd^{3+} ions belonging to the sublattices 1 and 2 are determined by the following expressions:

$$\begin{cases} B_{\text{eff}\,1\alpha} = B_\alpha + \kappa_{11\alpha} M_{1\alpha}^{Nd} + \kappa_{12\alpha} M_{2\alpha}^{Nd} + B_{ex}^{Nd}{}_{\alpha} \\ B_{\text{eff}\,2\alpha} = B_\alpha + \kappa_{11\alpha} M_{2\alpha}^{Nd} + \kappa_{12} M_{1\alpha}^{Nd} - B_{ex}^{Nd}{}_{\alpha} \end{cases} \qquad (2)$$

Here, M_1^{Nd} and M_2^{Nd} are the magnetic moments of the first (1) and the second (2) neodymium sublattices, respectively. Parameters κ_{11} and κ_{12} determine internal magnetic fields acting on the Nd^{3+} ion with a given magnetic moment, which are induced by Nd^{3+} ions with the same (κ_{11}) and opposite (κ_{12}) directions of their magnetic moments.

For compounds with a high concentration of neodymium, x=1, 0.75, 0.50, and 0.25, the contribution of the Nd subsystem describes well the Schottky anomaly in the C(T) dependence [11]. However, for compounds with low concentration, x≤0.05, the calculated contribution exceeds the experimental data. We assume that only a part of the nominal concentration of the neodymium contributes into the specific heat and magnetic susceptibility, and this part decreases with decreasing x. In according to this assumption, we calculate the contribution of the Nd subsystem into the total magnetic susceptibility and specific heat represented by thick solid lines in Fig.1 and Fig.3, respectively.

4.2 Contribution from chain breaks and ferrons

An additional contribution into specific heat that takes place at temperatures higher than the temperature of the Schottky maximum can be described by chain breaks. Uncontrollable nonmagnetic impurities can result in breaks in nickel chains and the formation of a set of chain segments. According to the valance-bond solid model (VBS) [14], each spin S=1 can be represented in the form of two spins S=½. Unpaired spins S = 1/2, which appear at the ends of chain segments, can interact with each other along the chain. This interaction causes a splitting of the fourfold degenerate level into a singlet (S = 0) and a triplet (S = 1) states. The splitting of the triplet into two sublevels is caused by an anisotropy of the Ni^{2+} ion. For the best agreement with the experimental data, we assume that the splitting reflecting interaction between end spins ½ depends on the temperature and this behavior is similar to the behavior of the Haldane gap in the ordered state. Such behavior has been explained in the framework of a mean-field model that considered Haldane chains in a staggered magnetic field created by the ordered rare-earth magnetic moments. Redistribution of the electrons on the energy sublevels

corresponding to chain segments gives a Schottky anomaly at 5 K in the specific heat and a maximum in the magnetic susceptibility at about 10 K. The contribution from chain breaks into the magnetic susceptibility and specific heat is represented by thin solid lines in Fig1 and Fig.3, respectively. A modeling points to the concentration of nonmagnetic impurities of about 3%.

Another additional contribution that cannot be described by the contribution of the Nd subsystem at the lowest temperatures can be explained by a small oxygen nonstoichiometry, resulting in the formation of holes in the 2*p* orbitals of the oxygen ions along a nickel chain [15, 16]. The holes have effective spins ½, as each $2p_z$ orbital containing a hole is occupied by a single electron. The interaction between Ni1 and Ni2 ions which surround a hole is realized by hopping of the hole with a spin S=1/2 from O to Ni1 and from Ni2 to O. This exchange interaction leads to a ferromagnetic coupling between the Ni ions. In the framework of the VBS model, a hole with S=1/2 provides a break in the VBS state of the S = 1 chain. The two Ni-ions, which are the nearest neighbors of the hole, have unpaired spins S=1/2. Thus, a spin bubble, named ferron, consists of three spins S=1/2, the central spin belonging to the oxygen hole. We have to take into account the interaction between two ferrons, because a single ferron does not give anomalies in the specific heat and magnetic susceptibility. Temperature changes in the population of the energy sublevels corresponding to the system of two ferrons give a maximum in the susceptibility at about 3 K and a Schottky anomaly in the specific heat at about 1 K. The modeling points to the concentration of ferrons of about 1%.

4.3 Magnetic ordering

The anomalies observed in the temperature dependencies of specific heat are explained by the contribution from the Ni chain breaks and ferrons, and also from the neodymium subsystem. We had to suppose that only a part of the nominal Nd concentration contributes. Although we checked the concentration of neodymium, we cannot exclude that the real Nd concentration was smaller than the nominal one. Possibly, a more thorough investigation of this point is necessary. Another reason can be the formation of magnetic clusters, inside of which the Nd ions interact with each other through the Ni chain (at the distance of correlation length).

The spectroscopic data and the presence of the Schottky anomaly in specific heat unambiguously point to a splitting of the Nd ground Kramers doublet and, hence, to the presence of an internal magnetic field. Such field could be a result of a magnetic ordering. Meanwhile, the residual splittings of the neodymium ground KD due to strong correlations in Haldane chains exist also in the paramagnetic phase of Nd_2BaNiO_5, giving rise to a “tail” of residual line splittings [12], see Inset to Fig. 4c. The internal field can result also from the short-range order, i.e., ordering inside the magnetic clusters.

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