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Ho^{3+} crystal-field levels, magnetic ordering, and magnetoelastic coupling in the chain nickelate Ho_2BaNiO_5

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ABSTRACT

Transmission spectroscopy data in wide spectral and temperature ranges are presented for Ho_2BaNiO_5. A quasi-doublet ground state of the non-Kramers Ho^{3+} ion, previously predicted theoretically, is confirmed experimentally for the first time. Its temperature-dependent splitting manifesting magnetic ordering at the Neél temperature $T_N = 49$ K is discussed in the frame of the perturbation and mean-field approaches. Holmium contribution into the magnetic susceptibility $\chi(T)$ and specific heat $C(T)$ is calculated using the spectroscopic data. The calculated contribution describes well experimental data available in literature. Analysis of shifts of the Ho^{3+} energy levels reveals magnetoelastic interactions in the antiferromagnetic state of Ho_2BaNiO_5.

1. Introduction

Ho_2BaNiO_5. is a magnetic compound with two interacting magnetic subsystems. One of them is a system of Haldane chains composed of spins $S = 1$ (Ni^{2+}), another one is a network of Ho^{3+} ions placed between the chains. The chains, in the absence of another magnetic subsystem (in the parent isostructural compound Y_2BaNiO_5), demonstrate strongly one-dimensional (1D) properties [1–5]. The presence of magnetic rare-earth (RE) ions between the chains in R_2BaNiO_5 (R = RE) leads to a 3D magnetic ordering at low temperatures [6–10] while 1D properties are still kept even in the antiferromagnetically (AFM) ordered state [11–14].

Ho_2BaNiO_5 has an orthorhombic structure (the space group *I*mmm) at room temperature, as was shown by X-ray diffraction, neutron scattering, and Raman spectroscopy [15–18], and preserves this structure at low temperatures, at least down to 2 K [17]. The main peculiarity of a crystallographic structure is the presence of well isolated chains of NiO_6 octahedra (see Fig. 1). HoO_7 capped prisms with the C_{2v} symmetry are situated between the chains. Ho_2BaNiO_5 orders antiferromagnetically at about 50 K [6,7,19–21]. Magnetic moments of both holmium and nickel ions are oriented predominantly along the *c* crystallographic axis [21,22]. The orientation of magnetic moments for different R_2BaNiO_5 compounds depends on a magnetic anisotropy of the R^{3+} ion. Such physically grounded conclusion was supported by the results of crystal-field (CF) calculations based on the spectroscopic data on R^{3+} ions in the chain nickelates [23,24]. Spectroscopic data for the Ho^{3+} ion in Ho_2BaNiO_5 were absent, except an incomplete information on the ground $^5I_8$ multiplet, with inelastic neutron scattering peaks at the energies 0, 1.3, 2.7, 11.6, and 15.1 meV (0, 10, 22, 93, and 120 cm^{-1}) being attributed to the holmium CF levels [20]. On the basis of the CF parameters extrapolated from the data on Nd_2BaNiO_5 and Er_2BaNiO_5, Ref. [23] predicted that the ground state of the Ho^{3+} ion is a quasi-doublet (QD) with a very small zero-field splitting $\Delta_i = 0.1$ cm^{-1} and that the next sublevel of the $^5I_8$ multiplet lies at about 80 cm^{-1} higher, which contradicts to Ref. [20]. Thus, additional experiments are needed to elucidate the energy structure of the ground as well as excited multiplets of the Ho^{3+} ion in Ho_2BaNiO_5. These data are also necessary to interpret low-temperature peculiarities in the magnetic susceptibility [7] and heat capacity [19], both of which demonstrate a strong contribution of holmium. Refs. [6,23,24] suggest that this contribution can be calculated using temperature-dependent positions of low-energy RE excitations. On the contrary, Ref. [25] proposes a model for describing the rise of $\chi(T)$ in the temperature range 5–15 K by a contribution of the Haldane gap. Thus, it is important to understand whether it is possible to describe a behavior of the magnetic susceptibility in the low-temperature range by a holmium contribution calculated with the use of experimentally determined CF energies of holmium or it is necessary to involve different models.

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Another interesting fact is that the RE nickelates R_2BaNiO_5 behave like multiferroic materials with a strong magnetoelectric (ME) coupling [25,26]. In particular, Ho_2BaNiO_5 demonstrates a linear ME effect which arises in the AFM state [25]. The reason for this could be magnetoelastic interactions leading to atomic displacements below T_N and, as a result, to the electric polarization. Ref. [17] clearly shows that cell parameters, bond lengths and angles change in the AFM state of Ho_2BaNiO_5, which points to magnetoelastic effects below T_N. One could await a change of the crystal field acting on the Ho^{3+} ions and corresponding changes in optical spectra.

In this paper the first, to the best of our knowledge, spectroscopic study of Ho^{3+} CF energies in Ho_2BaNiO_5 is presented. Wide spectral and temperature ranges were investigated. The CF energies for the ground multiplet of the Ho^{3+} ion in Ho_2BaNiO_5 are found. It is confirmed that the ground state of holmium is a QD. The temperature-dependent data on holmium CF energies are used to study a magnetic ordering and to explain low-temperature peculiarities in the magnetic susceptibility and heat capacity of Ho_2BaNiO_5. Shifts of energy levels up to 5 cm^{-1} at $T < T_N$ are attributed to a combined action of an internal magnetic field and magnetoelastic interactions arising in the AFM state.

2. Experiment

X-ray single phase polycrystalline samples of Ho_2BaNiO_5 were prepared by solid state reactions as described in Ref. [6]. Powder was mixed with spectroscopic grade pure KBr and pressed into pellets. Transmission spectra were measured on a Bruker IFS125HR spectrometer with the use of CaF_2/InSb and Quartz/Si beamsplitter/detector configurations for different spectral ranges. Low temperatures were obtained using a Cryomech PT403 closed-cycle cryostat.

3. Experimental results

Fig. 2 shows the energy-level scheme for the Ho^{3+} ion, together with the transmission spectrum of Ho_2BaNiO_5 at 5 K. The $4f^{10}$ electronic configuration of the free Ho^{3+} ion is split into terms and multiplets due to the electrostatic and spin–orbit interactions, respectively (Fig. 2a). For RE elements in a crystalline matrix, the multiplet sequence does not change. Comparison of the measured spectrum (Fig. 2b) with the data for the holmium ion from the classical Dieke scheme [27] shows that the multiplets can be easily identified. Arrows in the scheme of Fig. 2c indicate several possible transitions. Each transition is denoted by two symbols corresponding to the initial and final states of this transition, e.g., 2a, or 1b. Dashed arrows are used for the transitions originating from excited sublevels of the ground multiplet. Spectral lines corresponding to these transitions vanish at low enough temperature when the initial state of the transition is depopulated according to the Boltzman distribution.

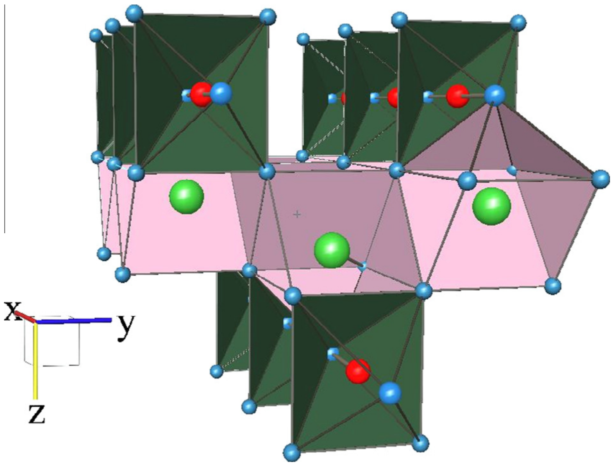

Fig. 1. Fragment of the *I*mmm nickelate structure. *R* – big green balls, Ni – middle-size red balls, O – small blue balls. Chains of NiO_6 flattened octahedra running along the crystallographic *a*-axis are interconnected through RO_7 capped prisms with the C_{2v} symmetry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

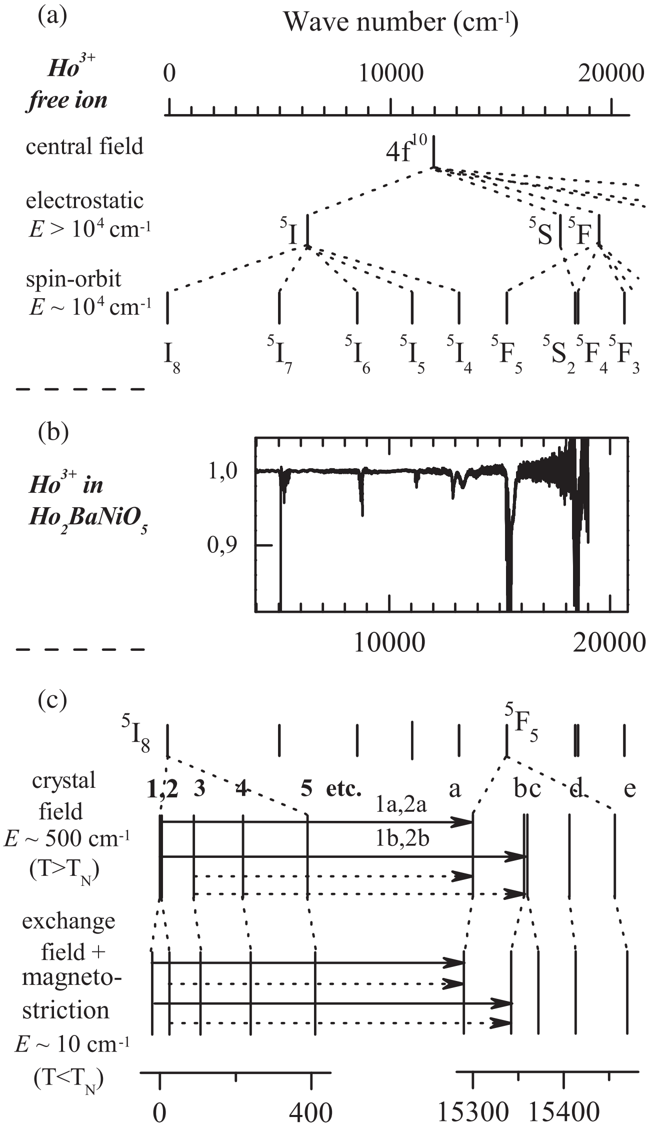

Fig. 2. (a) Energy-level scheme for the free Ho^{3+} ion, (b) Ho^{3+} absorption in Ho_2BaNiO_5 at 5 K, (c) energy-level scheme for CF levels and the influence of an effective magnetic field and magnetostriction. Arrows indicate some optical transitions (see the text).

Fig. 3 shows transmission spectra of Ho_2BaNiO_5 in the region of the $^5I_8 \rightarrow {}^5F_5$ transition of the Ho^{3+} ion at different temperatures. The changes presented in this figure are typical for all multiplets studied ($^5F_5$, $^5I_7$, $^5I_6$, $^5I_5$, $^5I_4$). First, there are spectral lines that vanish at low temperatures. They belong to the transitions originating from the excited CF-levels of the ground multiplet (they are marked by black arrows). Analysis of temperature-dependent spectra of all multiplets enabled us to find the following CF energies for the holmium ground $^5I_8$ multiplet: 0, 90, 100, 120, 175, 220, 290, and 390 cm^{-1}. CF energies for excited multiplets were also found, they will be discussed in another publication, together with CF calculations. Second, at temperatures $T < T_N$ the spectral lines split and shift, which is a signature of a magnetic phase transition. The low-frequency component of each split line diminishes in intensity with lowering the temperature and vanishes at the lowest temperatures (see the low-frequency components of the lines 1e and 1g in Fig. 3), which is an indication that the initial level of a given transition is depopulated.

Symmetry analysis for the holmium site in Ho_2BaNiO_5 (C_{2v}) shows that the states of the non-Kramers Ho^{3+} ion are singlets characterized by four different irreducible representations (IrR), Γ_1, Γ_2, Γ_3, and Γ_4 (the analysis was performed using tables from Refs. [28,29]). Table 1 shows how a level with the total momentum $\boldsymbol{J}$ splits in a crystal field of the C_{2v} symmetry. Selection rules for electric dipole (ED) and magnetic dipole (MD) transitions are summarized in Table 2. In particular, it follows from this Table that all ED transitions are allowed except $\Gamma_1 \leftrightarrow \Gamma_3$ and $\Gamma_2 \leftrightarrow \Gamma_4$ ones.