Effect of magnetic ordering of Dy_2BaNiO_5 on the crystal-field levels of dysprosium: optical spectroscopy of f-f transitions

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Abstract. Optical transmission spectroscopy study of the Haldane magnet Dy_2BaNiO_5 was performed in the region of f-f transitions of the Dy^{3+} ion in a wide range of temperatures (5-300 K). At temperatures lower than T_N (59 K), Kramers doublets of the rare-earth ion split. Spectroscopic data obtained were used to calculate the Schottky-type anomaly in the temperature dependence of the magnetic susceptibility of Dy_2BaNiO_5 and to model the experimental data available in literature. Anomalous behavior of crystal-field energies of the Dy^{3+} ion was attributed to the magnetoelectric interactions.

Dysprosium nickelate Dy_2BaNiO_5 belongs to the family of rare-earth (RE) chain nickelates R_2BaNiO_5 (R=RE), well-known as model compounds for studying Haldane magnetism [1,2]. In Dy_2BaNiO_5, antiferromagnetic (AFM) ordering arises at $T_N = 59$ K [3,4] due to dysprosium-mediated interaction between nickel S=1 chains. Temperature dependence of the magnetic susceptibility $\chi(T)$ of Dy_2BaNiO_5 has a broad maximum at $T_m = 45$ K [5], attributed to a dysprosium contribution. Shottky-type anomaly in the $\chi(T)$ dependence can be calculated directly from spectroscopic data on the RE ground-doublet splitiing [6,7], however, such data are not available in the literature. According to recent studies, Dy_2BaNiO_5 demonstrates multiferroic behavior [8], spontaneous electric polarization **P** emerges at $T<T_N$. In this work, we study the temperature behavior of crystal-field (CF) levels (Kramers doublets) of the Dy^{3+} ion by means of optical spectroscopy, with the aim to extract information on low-energy CF-excitations of the dysprosium ion and to calculate the dysprosium contribution into the magnetic susceptibility of Dy_2BaNiO_5. Another goal was to look for spectroscopic effects related to the appearance of **P** in the AFM phase.

Optical transmittance spectra of polycrystalline Dy_2BaNiO_5 were measured in a wide spectral range (3000 – 15000 cm^{-1}) comprising several multiplets of the Dy^{3+} ion, with the use of a BRUKER IFS125HR Fourier spectrometer. To get low temperatures, a closed-cycle optical cryostat CRYOMECH PT403 was used. The analysis of temperature-dependent transmission spectra enabled us to find the following CF energies (in cm^{-1}) for different multiplets: $^6H_{15/2}$ (0, 150, 275), $^6H_{13/2}$ (3565, 3670, 3690, 3770, 3810, 3860, 3910), $^6H_{11/2}$ (5978, 6026, 6063 6070, 6109), $^6H_{9/2}$+$^6F_{11/2}$ (7755, 7788, 7824, 7923, 7946, 7962,

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7985, 8033, 8135),), $^6H_{7/2}+^6F_{9/2}$ (9138, 9173, 9220, 9274, 9343, 9366, 9422, 9518), $^6F_{7/2}$ (11095, 11170, 111925, 11258), $^6F_{5/2}$ (12505, 12525, 12630), $^6F_{3/2}+^6F_{1/2}$ (13353). In particular, the ground Kramers doublet is separated by a gap from the excited states. Thus, a model of an isolated ground doublet [6,7] can be used for describing thermodynamic properties of Dy_2BaNiO_5.

The observed splitting of Kramers doublets (Fig. 1) confirms a magnetic ordering of the crystal at $T_N = 59$ K. For modeling of the dysprosium contribution to the magnetic susceptibility $\chi(T)$ of Dy_2BaNiO_5 we have utilized experimentally obtained temperature-dependent splitting of the ground Kramers doublet $\Delta_0(T)$, which reaches the value of 39 cm^{-1} at 5 K. The results of modeling lead us to a conclusion that the low-temperature magnetic susceptibility of Dy_2BaNiO_5 is determined by the dysprosium contribution, while the one-dimensional contribution of the nickel chains is much smaller.

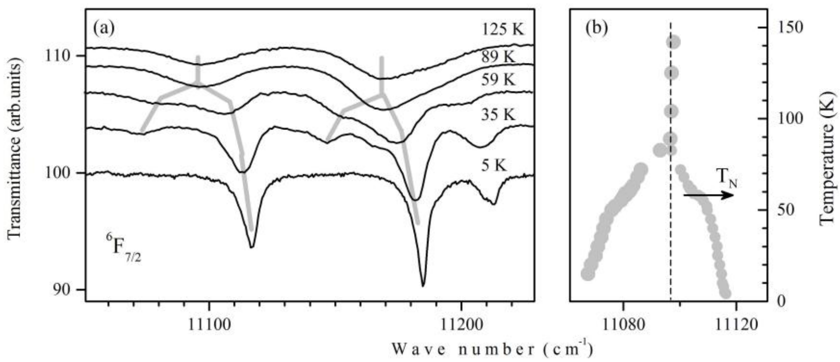

Fig. 1. (a) Transmission spectra in the region of $^6F_{7/2}$ multiplet of Dy^{3+} ion in Dy_2BaNiO_5 at different temperatures. Grey lines show schematically line splittings. (b) Positions of line 11096 cm^{-1} and its split components as a function of temperature. Vertical dashed line is drawn to underline asymmetrical character of splitting.

Unusual behavior of the dysprosium CF energies in Dy_2BaNiO was detected in the temperature range lower than T_N. All CF levels experience a shift (up to 10 cm^{-1}) from their positions at T_N (see, e.g., Fig. 1). Such behavior can be explained as being due to the spontaneous electric polarization that appears in the temperature range discussed [8]. Redistribution of the charge density influences the crystal field acting on dysprosium and leads to a renormalization of CF self-energies.

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