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Raman scattering on electronic levels in rare-earth iron borates RFe$_3$(BO$_3$)$_4$

S.A. Klimin*, and M.N. Popova

Institute for Spectroscopy RAS, 108840 Troitsk, Moscow, Russia

Abstract. We have performed a Raman scattering study for single crystals of the rare-earth (RE) iron borates RFe$_3$(BO$_3$)$_4$, R = Nd, Tb, Pr, in the range of temperatures 3-300 K. Electronic Raman scattering on the 4f levels of RE ions was registered, which enabled us to specify the schemes of crystal-field levels within ground multiplets of the RE ions. A splitting of the Kramers doublets in electronic Raman spectra of the neodymium iron borate testifies a magnetic ordering of the compound. Raman scattering from a coupled mode of the spin oscillations of the Fe and Nd subsystems was observed in NdFe$_3$(BO$_3$)$_4$.

The rare-earth (RE) iron borates RFe$_3$(BO$_3$)$_4$ are widely studied by different methods due to their multiferroicity. They are interesting both as promising compounds and as model systems for studying mechanism of interactions between different degrees of freedom such as charge, magnetic, lattice, and electronic ones [1-4]. All the iron borates experience phase transition into antiferromagnetic phase at low temperatures in the range 32-39 K. Precise information on the energies of crystal-field (CF) levels for the ground multiplet of the RE ion is needed to interpret reliably magnetic, magnetoelectric, and thermal properties of these compounds, as well as the effects of electron-phonon and electron-magnon interactions. Optical IR transmission spectroscopy gives limited information on the CF structure of the ground multiplet, as the population of excited levels is small, while Raman spectroscopy does not suffer from this restriction. In this work, we study Raman scattering on electronic levels of RE iron borates with R = Nd, Tb, Pr.

Raman spectra in a wide temperature range (3-300 K) were measured using Jobin-Yvon T64000 spectrometer. At low temperatures, in the Raman spectra registered, in addition to phonon peaks, spectral lines are present related to two-magnon as well as to electronic scattering. We have used several excitation wavelengths (532, 514.5 и 488 nm) to separate a scattered signal from a luminescent one.

Several lines found in the Raman spectra of iron borates were attributed to the electronic scattering on the crystal-field levels of RE ions, namely, 201 см$^{-1}$ for Tb^{3+}, 197 см$^{-1}$ for Pr^{3+}, and 140 and 220 см$^{-1}$ for Nd^{3+}. At the temperatures lower than the temperature of an antiferromagnetic ordering of NdFe$_3$(BO$_3$)$_4$, T_N = 33 K, a new peak arises in the polarization geometry zx due to the scattering on the upper component of the split ground Kramers doublet of the Nd^{3+} ion (Fig. 1). This line moves to higher energy values with cooling and reaches 11 см$^{-1}$ at T ≈ 5 K. This value differs from the value Δ_0 = 8.8 см$^{-1}$ for

* Corresponding author: klimin@isan.troitsk.ru

the splitting of the ground Kramers doublet of the Nd^{3+} ion found by optical IR-study of $NdFe_3(BO_3)_4$ [5], while it is in a good agreement with the data obtained by submillimeter spectroscopy [6]. Similarly to the case of submillimeter radiation incident on the crystal, in the process of Raman scattering on 4f electronic CF levels, a new 4f-excitation appears in the crystal. This excitation interacts with close in energy antiferromagnetic mode of Fe-magnetic subsystem, which leads to the formation of coupled modes for the vibrations of the spins of Fe- and Nd-subsystems. Renormalization of frequencies [6,7] is responsible for the observed phenomenon.

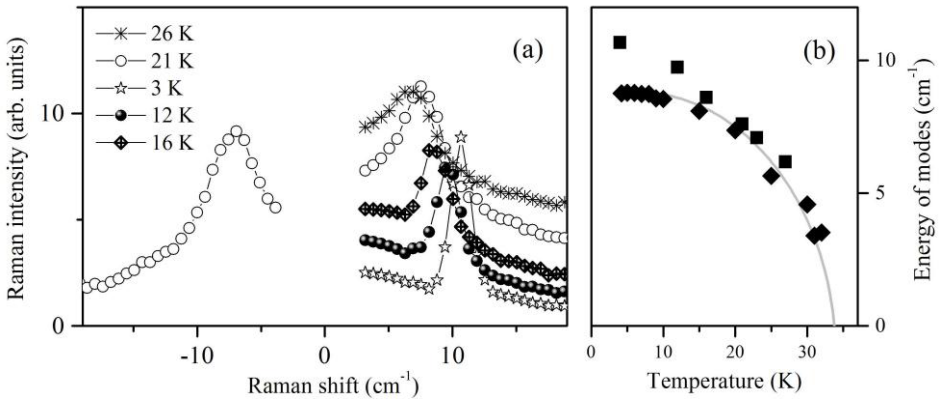

Fig. 1 (a) Raman spectra at different temperatures lower than T_N. Anti-Stokes component is shown confirming the origin of a peak presented. (b) Data on the splitting of ground Kramers doublet of Nd^{3+} ion (rhombs) [5] and the energy of the Raman mode (squares, this study) as a functions of temperature. Gray curve is guided to the eye.

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