Raman Study of the Rare-Earth Binary Ferroborate $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ Single Crystal

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We report comprehensive Raman scattering measurements on a single crystal of binary ferroborate $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ in the temperature range of 7 – 295 K with 532 nm (~18979 cm^{-1}) laser excitation. The performed analysis of polarized Raman spectra revealed the bands assigned to phonon, magnetic and electronic excitations. Temperature evolution of these quasi-particle excitations has allowed us to ascertain the intricate coupling and interplay between lattice, magnetic, and electronic degrees of freedom. Analysis of the measured Raman spectra made it possible to identify all $A1$ and E phonon modes of predicted by the group theoretical analysis. The splitting energies between the LO and TO components of the polar E phonons were determined. Below the temperature of magnetic ordering of the Fe-sublattice, T_N, we have revealed a multiple peaked two-magnon excitation. Analyzing the temperature evolution of low-frequency modes in the spectra, we also identified modes that are associated with electronic transitions between the crystal field (CF) levels of the Nd^{3+} ground-state $^4I_{9/2}$ and of the Dy^{3+} ground-state $^6H_{15/2}$ multiplets. In addition to the already known temperatures of magnetic transitions, analysis of the temperature behavior of low-frequency phonon and electronic excitations made it possible to establish a temperature T^* = 100 K, presumably associated with local distortions of the crystal lattice. The presence of this temperature is confirmed by our ultrasound study. A group of intense bands observed in the frequency range of 1700 – 2200 cm^{-1} has been associated to the mixed low-lying electronic Raman transitions $^4I_{9/2}\rightarrow{}^4I_{11/2}$ and the high-energy luminescence ones $^4G_{5/2}+{}^2G_{7/2}\rightarrow{}^4I_{9/2}$ in the Nd^{3+} ion.

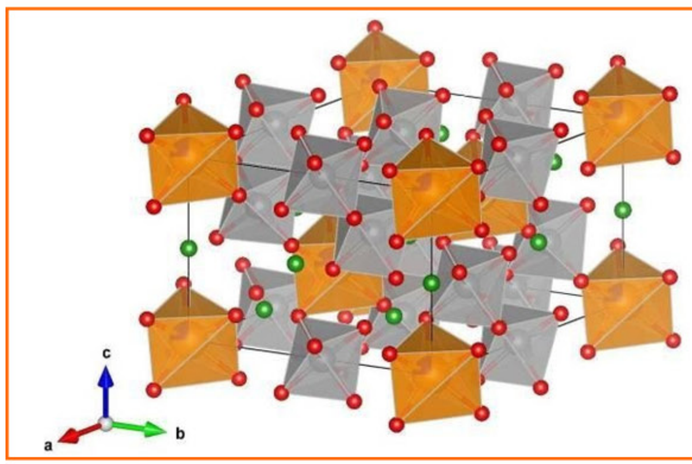

Fig.1. The crystalline structure of the $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ unit cell. The FeO_6 octahedra and $Nd_{0.75}/Dy_{0.25}O_6$ trigonal prisms are presented in grey and orange colors, respectively. O and B atoms are shown in red and green colors, respectively.

The first results from the study of $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ (trigonal space group $R32$) revealed two magnetic phase transitions: first at T_N = 32 K, which was attributed to a transition into the antiferromagnetic, easy-plane state, and second at T_R = 25 K which corresponds to a spin-reorientation transition into the easy-axis state. The behavior of the magnetization and specific heat of this compound demonstrated the presence of four features at T_N = 32 K, T_1 = 24 K, T_2 = 22 K, and T_3 = 16 K both in the temperature dependence of the magnetization and of the specific heat. For the high-temperature structure, the theory-group analysis gives Γvibr=7A_1(Raman)+12A_2(IR)+19E(Raman) optical vibrational modes, where the number of external and internal (related to the vibrations of BO_3 groups) vibrational modes is =3A_1+11E and =4A_1+8E, respectively. The doubly degenerated E modes are polar and both IR and Raman active.

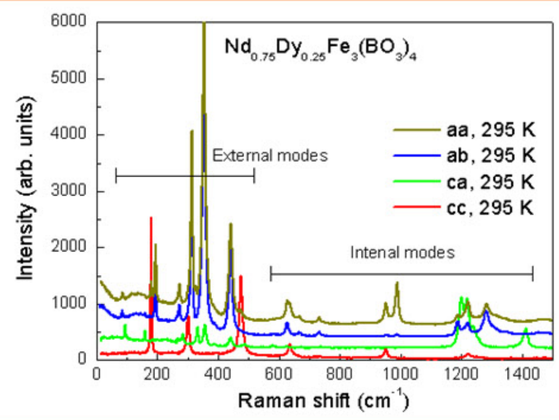

Fig. 2. The room-temperature Raman spectra of $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ taken in the different polarization configurations. The regions assigned to the external optical vibrations and the internal BO_3 vibrations are indicated by the horizontal bars.

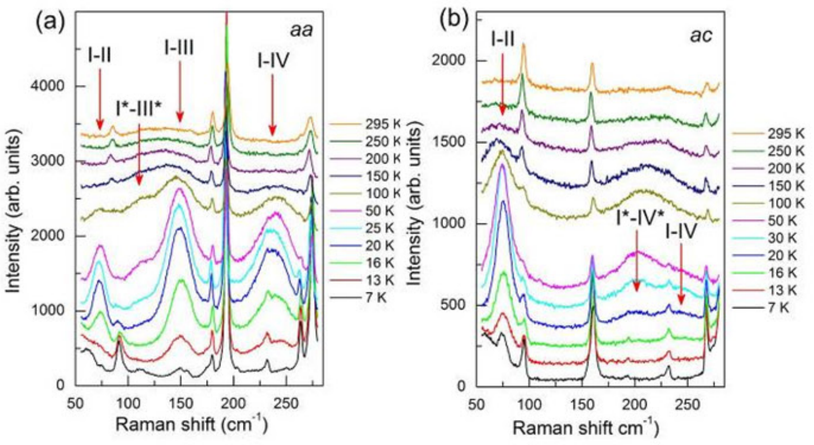

Fig. 3. (a) Temperature dependent Raman spectra of $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ measured in the frequency region of the low-frequency crystal field excitation in the *aa* (a) and *ac* (b) scattering configurations.

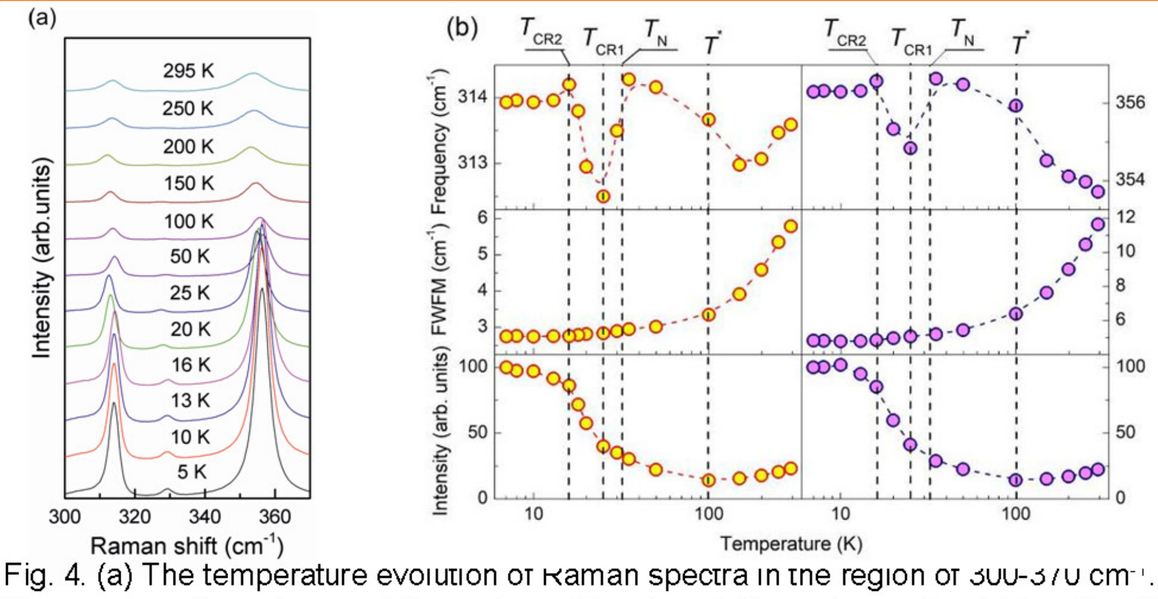

Fig. 4. (a) The temperature evolution of Raman spectra in the region of 300-370 cm^{-1}. (b) Temperature dependence of the peak position, linewidth, and normalized intensity of two external phonon modes (313.9 and 356.8 cm^{-1}) of $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$. The vertical dashed lines indicate the magnetic transitions, T_N, T_{CR1}, and T_{CR2} and structural distortion, T^* temperatures.

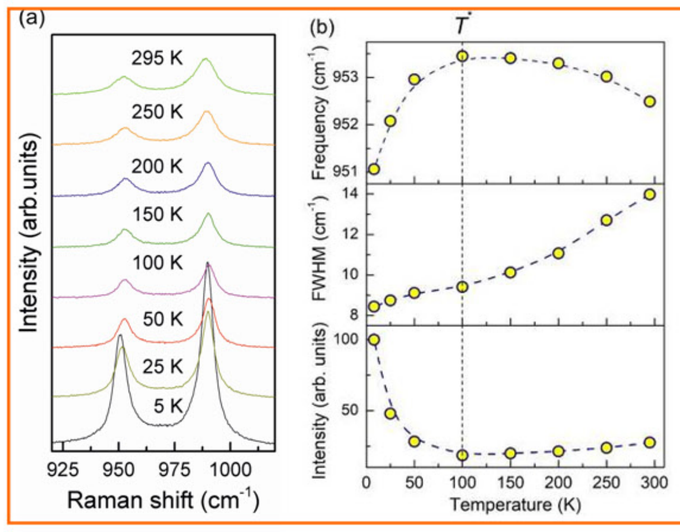

Fig. 5. (a) The temperature dependent Raman spectra in the region of 920-1020 cm^{-1}. (b) Temperature dependence of frequency, linewidth, and normalized intensity of the internal BO_3 phonon mode at 952 cm^{-1}. The vertical dashed line indicates the pronounced structural distortion T^* temperature.

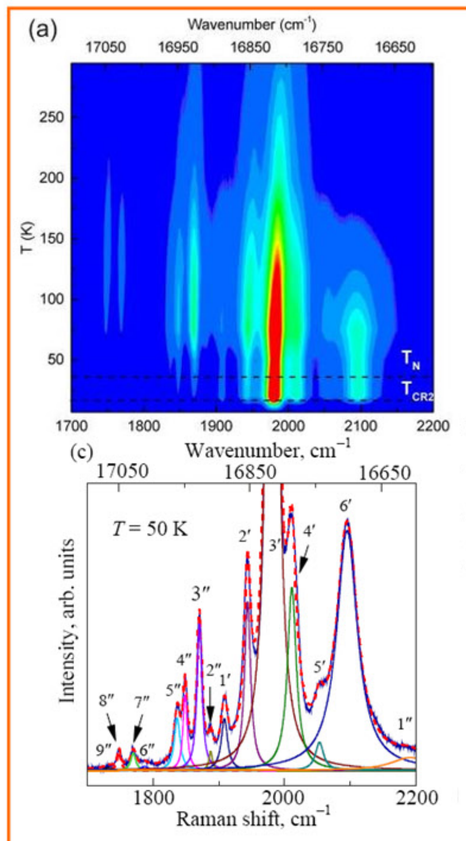

Fig. 6 (a) Color contour plot of the electronic bands' intensity in the temperature dependent Raman shift plane. (b) Temperature evolution of Raman spectra ranging from 1700 to 2200 cm^{-1}. (c) Raman spectrum taken at T=50 K is fitted to a sum of Lorentzian profiles. The lines labeled 1' to 6' may be assigned to the Raman $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transitions and the lines marked 1'' to 9'' may be assigned to the luminescence transitions $^4G_{5/2}+{}^2G_{7/2} \rightarrow {}^4I_{9/2}$.

	Compound, literature data	$\Delta = E_i - E_1$, cm^{-1}
$^4I_{9/2}$, Nd^{3+}	Theory; $NdFe_3(BO_3)_4$	I - 0, II - 66, III - 141, IV - 220, V - 310
	Expt.; $NdFe_3(BO_3)_4$	I - 0, II - 65, III - 141, IV - 221, V - 322
	Theory; $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$	I - 0, II - 79.2, III - 165.8, IV - 261
$^6H_{15/2}$, Dy^{3+}	Theory; $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$	I* - 0, II* - 21.9, III* - 108.6, IV* - 207

	$Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$, T = 50 K present studies	$NdFe_3(BO_3)_4$, T = 50 K previous studies
N	$^4I_{9/2} \rightarrow {}^4I_{11/2}$	
1'	1908	1949
2'	1944	1955
3'	1981	1979
4'	2011	2053
5'	2053	2087
6'	2095	2131

CONCLUSION

In summary, we have presented the Raman scattering study of the $Nd_{0.75}Dy_{0.25}Fe_3(BO_3)_4$ single crystal in wide frequency region of 12–2500 cm^{-1} at temperatures 7–295 K. The performed detailed analysis of polarized Raman spectra revealed the bands assigned to phonon, magnetic and electronic excitations. All A_1 and E phonon modes, predicted by the group-theory analysis, were revealed in Raman spectra and have been classified into either internal or external modes. Phonon Raman scattering indicates strong spin-lattice coupling by revealing distinct anomalies at temperatures T^*, T_{CR1}, T_{CR2}, and T_N. The observed in the spectra bands at 73.4, 149, and 237.7 cm^{-1} have been assigned to electronic transitions between the CF levels of the Nd^{3+} ground-state $^4I_{9/2}$ multiplet and bands at 111.9 and 201.5 cm^{-1} - to the transitions between the CF levels of the Dy^{3+} ground-state $^6H_{15/2}$ multiplet. A group of intense bands observed in the frequency range of 1700 – 2200 cm^{-1} has been associated to the mixed electronic Raman $^4I_{11/2}\rightarrow{}^4I_{9/2}$ and luminescence $^4G_{5/2}+{}^2G_{7/2}\rightarrow{}^4I_{9/2}$ transitions in the Nd^{3+} ion which demonstrate different temperature behavior. The complicated temperature evolution of the high-frequency electronic bands is explained by the strong exchange competition coupling of the magnetic sublattices formed by the different types of the magnetic ions below T_N.