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Magnetic ordering of $NdFe_3(BO_3)_4$ studied by infrared absorption spectroscopy

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Abstract

We report the first measurements of the optical spectra of $NdFe_3(BO_3)_4$, a promising material for optoelectronics. Exchange splitting of Nd^{3+} spectral lines due to magnetic interactions in a magnetically ordered state was observed. The temperature dependences of the exchange splitting and of the linewidth point to the temperature $T_c = 33 \pm 1$ K of the magnetic ordering in both iron and neodymium magnetic subsystems.

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Keywords: Ferroborates; Fourier-transform spectroscopy; Magnetic ordering

1. Introduction

The family of the borates $RM_3(BO_3)_4$ (R = Y, La–Lu, M = Al, Ga, Cr, Fe, Sc) is interesting because of possible applications in quantum- and optoelectronics and nonlinear optics. Nd-doped $YAl_3(BO_3)_4$ (YAB) or $GdAl_3(BO_3)_4$ (GAB) crystals and the concentrated crystal $NdAl_3(BO_3)_4$ (NAB) were shown to be excellent self-frequency-doubling, self-sum-frequency-mixing and, respectively, microchip laser materials (see, e.g., [1–3]). These crystals combine good physical and chemical properties, high gain, and outstanding nonlinear optical properties. A substitution of the magnetic Fe^{3+} ion for a nonmagnetic Al^{3+} may result in new applications, e.g., for Faraday devices.

The structure of $RM_3(BO_3)_4$ borates belongs to the structural type of the mineral huntite $CaMg_3(BO_3)_4$. It was described in detail in, e.g., Ref. [4]. The R^{3+} ion is coordinated by six oxygen ions forming an isolated distorted trigonal prism. M^{3+} ions are inside MO_6 octahedra. These octahedra share edges and form helicoidal chains along the c-axis. Three chains are interconnected by one common RO_6 prism (see Fig. 1). For $NdFe_3(BO_3)_4$, the space group is D_3^7 (R32), the local point symmetry group for Nd^{3+} ions is D_3.

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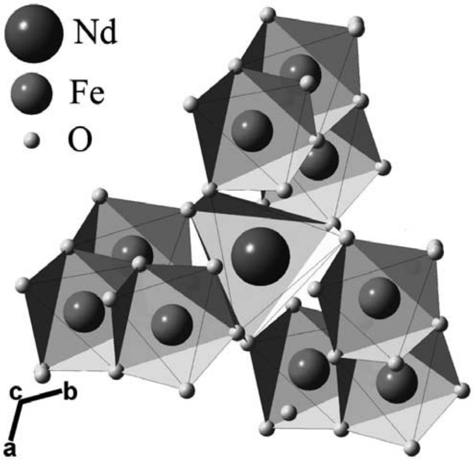

Fig. 1. Structure of $NdFe_3(BO_3)_4$. A fragment of the *ab* projection showing how the NdO_6 prism interconnects three helicoidal chains of FeO_6 octahedra. Boron atoms are not shown.

The structure and magnetic susceptibility of the $RFe_3(BO_3)_4$, R = Y, La, and Nd, single crystals was studied in Ref. [4]. For all the three crystals, magnetic susceptibility exhibited a maximum at the temperature ~ 35 K and a peculiarity at ~ 260 K. One more maximum at $T \approx 6$ K was found for the Nd compound. The maxima at 35 K have been interpreted as being due to one-dimensional correlations within chains formed by FeO_6 octahedra, while the peculiarity at 6 K in $NdFe_3(BO_3)_4$ has been attributed to a three-dimensional ordering of both Fe and Nd magnetic subsystems [4].

In this Letter, we report on the spectroscopic study of a magnetic ordering in $NdFe_3(BO_3)_4$. To our knowledge, it is also the first spectroscopic study of this material.

2. Experiment

Single crystals of $NdFe_3(BO_3)_4$, $GdFe_3(BO_3)_4$, and $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$ were grown by a group method [5] using a $K_2Mo_3O_{10}$-based flux, as described in Ref. [6]. The seeds were received by spontaneous nucleation from the same flux. Big (10–15 mm) transparent single crystals of ferroborates were green in color and had good optical quality. Thin plates 5 × 10 mm with different thickness (between 2.2 mm and 150 μm) were prepared for optical measurements. The longest edge of a plate was oriented along the *c*-axis. The samples were put into a helium-vapor cryostat with a variable temperature. Optical absorption spectra in the spectral region 4000–14000 cm^{-1} at a resolution 4–0.15 cm^{-1} were registered by a Fourier-transform spectrometer BOMEM DA3.002 with InSb liquid nitrogen cooled detector, at the sample temperatures between 4.2 and 300 K.

3. Results and discussion

Fig. 2 shows the room-temperature transmission spectra of $NdFe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$. A Gd-sample was studied for a comparison. The Gd^{3+} ion has no energy levels in the whole spectral range up to the ultraviolet region ($\sim 33\,000$ cm^{-1}). Both samples exhibit a strong broad absorption band centered at about $11\,500$ cm^{-1}, due to d–d transitions in the Fe^{3+} ion. $NdFe_3(BO_3)_4$ demonstrates also additional absorption bands at about 6000, 12 500, and 13 400 cm^{-1}, due to f–f optical transitions within the Nd^{3+} ion. In this work, we studied in more detail the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition at about 6000 cm^{-1} that falls into a transparency window of the ferroborate matrix and is not saturated even in the concentrated compound.

Fig. 3 shows the transmission of $NdFe_3(BO_3)_4$ in this spectral region at different temperatures. Spectral lines narrow gradually with decreasing the temperature from 300 K to about 40 K and several lines disappear. This freezing-out of several lines corresponds to an emptying of excited Stark sublevels of the ground level $^4I_{9/2}$. The energies of the lowest levels as determined from our spectra are given in Table 1. The lines that remain at low temperatures are due to transitions from the ground state to the Stark sublevels of the level $^4I_{15/2}$. For an ion with an odd number of electrons, like Nd^{3+}, the crystal field of a symmetry lower than cubic splits a level with a given value of momentum J into $(J + \frac{1}{2})$ Kramers doublets. Thus, one should await 8 Stark sublevels for the level $^4I_{15/2}$. However, only 5 spectral lines are observed in the spectral region of the transition $^4I_{9/2} \rightarrow {}^4I_{15/2}$ at 40 K. With further decreasing the temperature, a growing splitting of the lowest-frequency spectral line 5877 cm^{-1} into several components is clearly observed (see Fig. 2). The lines with higher frequencies are strongly broadened

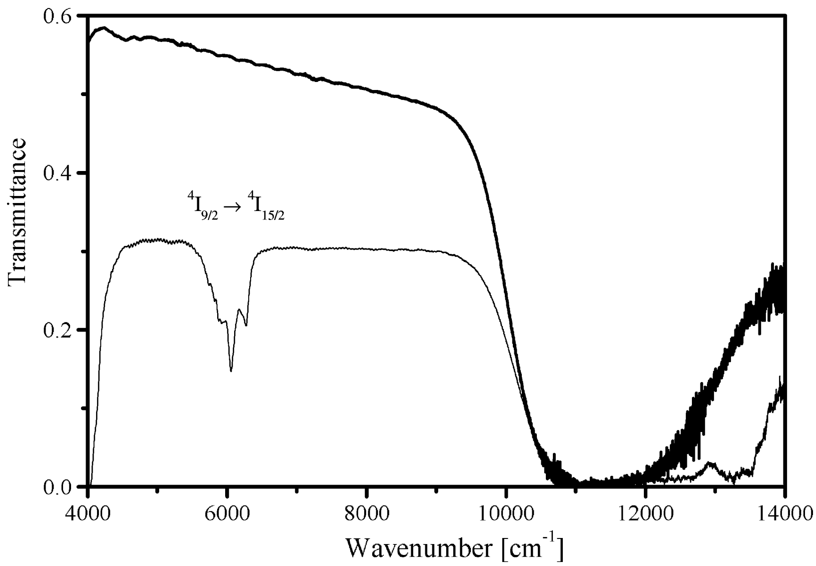

Fig. 2. Room-temperature transmission spectra of $NdFe_3(BO_3)_4$ (thin line) and $GdFe_3(BO_3)_4$ (thick line).

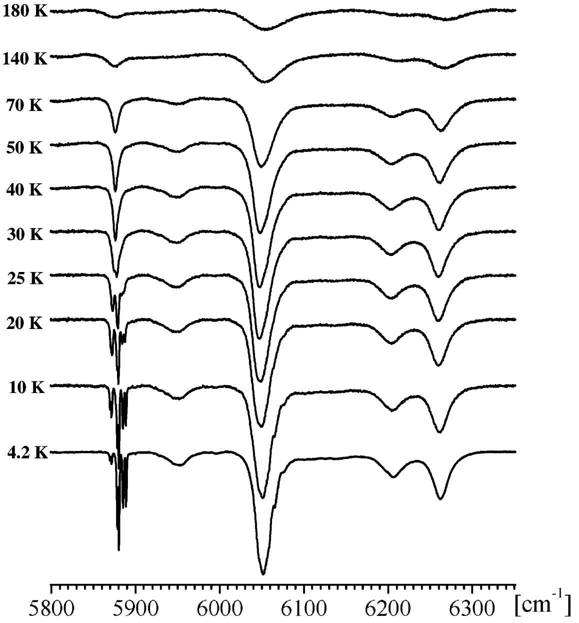

Fig. 3. Transmission spectra of $NdFe_3(BO_3)_4$ in the region of the $^4I_{9/2} \to {}^4I_{15/2}$ transition at different temperatures.

Table 1
Experimentally measured energies E and exchange splittings Δ at 4.2 K of $NdFe_3(BO_3)_4$ and $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$

$^{2S+1}L_J$	$Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$	$NdFe_3(BO_3)_4$	
	E (cm^{-1})	E (cm^{-1})	Δ (cm^{-1})
$^4I_{9/2}$	0	0	8.8
	49	51	
		145	
		221	
$^4I_{15/2}$	5847	5880	1.8
	5858	5887	3.5
	5937	5951	
	6065		
	6070	6051*	
	6087		
	6223	6206	
	6281	6262	

* A center of three close levels.

by phonon relaxation and do not show any clearly resolved structure.

The splitting of spectral lines may occur due to (i) structural changes and appearance of new structural positions for Nd^{3+} or (ii) magnetic ordering that causes the exchange splitting of Kramers doublets. In the case (i), the number of components of a split spectral line and their relative intensities correspond to the number of different structural sites and their relative quantity. In the case (ii), a spectral line splits into four components, as shown in the scheme of Fig. 4, and two of them freeze out with decreasing the temperature. Fig. 5 shows the absorption line 5877 cm^{-1} at different temperatures in more detail. Its temperature behavior is in accordance with the

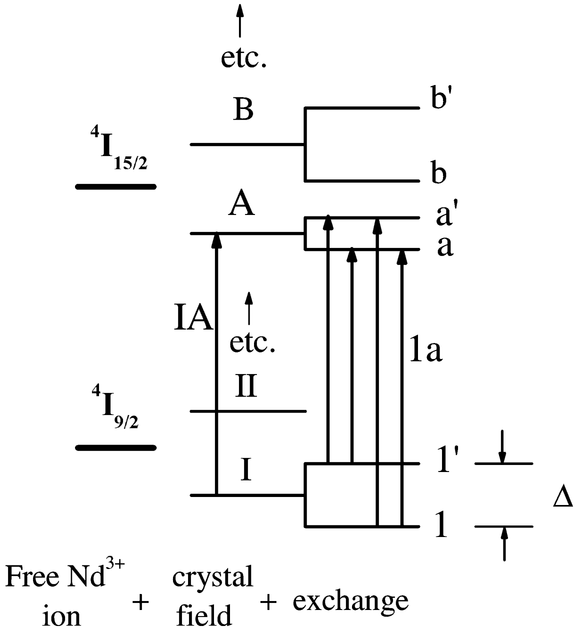

Fig. 4. Stark and exchange splittings of energy levels of the free Nd^{3+} ion caused by a crystal field and, respectively, magnetic interactions in a magnetically ordered state.

case (ii) provided there are two close Stark sublevels split by magnetic interactions. Such an interpretation is confirmed by a comparison with the spectra of Nd^{3+} in nonmagnetic $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$ that has the same crystal structure [3]. Fig. 6 presents the spectra of both $NdFe_3(BO_3)_4$ and $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$ at 70 and 4.2 K. The spectra are similar. In the low-temperature spectrum of $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$ the lowest-frequency crystal-field doublet is clearly seen. Also, the line at about 6070 cm^{-1} is a triplet. Table 1 summarizes the energies of Stark sublevels of Nd^{3+} in both compounds and the exchange splittings measured from the spectra of $NdFe_3(BO_3)_4$.

Fig. 7 displays the temperature dependence of the ground-state splitting of $NdFe_3(BO_3)_4$. It shows that a magnetic ordering occurs as a second order phase transition at $T_c \approx 33 \pm 1$ K. Simultaneously, the Nd^{3+} spectral lines strongly narrow (Fig. 7) which points to a simultaneous ordering of both iron and neodymium magnetic systems (see, e.g., Ref. [7]).

Thus, our spectral measurements show unambiguously that the maximum at 32 K in the $\chi(T)$ curve [4] corresponds to the three-dimensional antiferromagnetic ordering of $NdFe_3(BO_3)_4$.

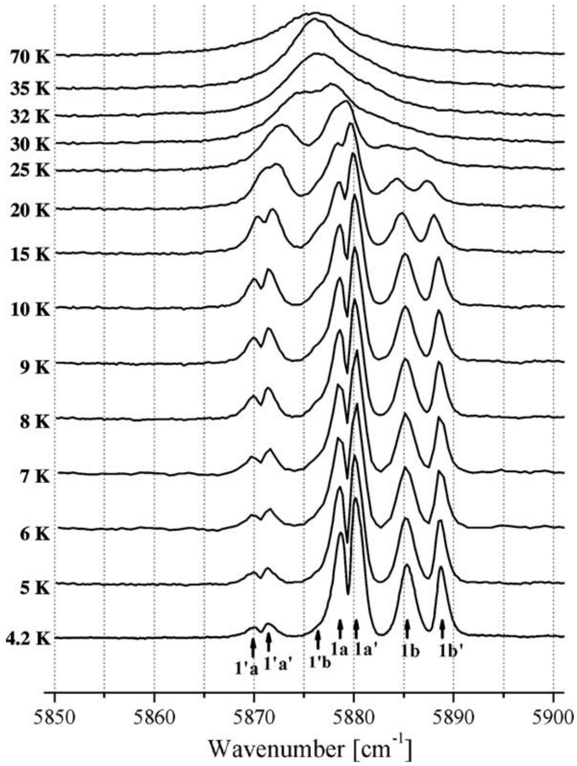

Fig. 5. Absorption line due to the transition from the ground level of $NdFe_3(BO_3)_4$ to the lowest energy levels of ${}^4I_{15/2}$ at different temperatures. Components of the lines split in a magnetically ordered state are labeled according to the scheme of Fig. 4.

We did not find any additional spectral peculiarities at lower temperatures, in particular, in the vicinity of the temperature 6 K of the second maximum in $\chi(T)$ curve of Ref. [4]. To our mind, this maximum might be caused not by a phase transition but by an emptying of the upper component of the rare-earth Kramers doublet split by the exchange interaction with neighboring iron ions, analogously to the case of Er_2BaNiO_5 [8]. A simple consideration results in the following relation for the temperature $T_{\max}$ of this maximum, in the case of well-isolated ground state [8]

$$kT_{\max} = \frac{\Delta}{1.54},$$

where Δ is the ground state exchange splitting (in cm^{-1}). For $NdFe_3(BO_3)_4$, $\Delta = 8.8\ cm^{-1}$ which results in $T_{\max} \approx 8$ K, close to the $T_{\max} \approx 6$ K found from the magnetic susceptibility measurements.

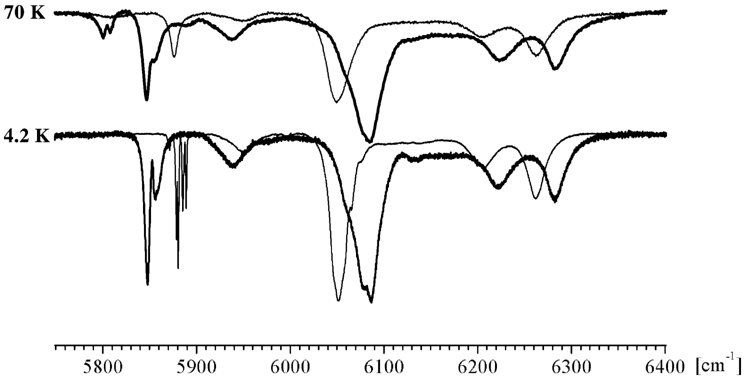

Fig. 6. Transmission spectra of $NdFe_3(BO_3)_4$ (thin lines) and $Nd_{0.1}Gd_{0.9}Al_3(BO_3)_4$ (thick lines) in the region of the $^4I_{9/2} \to {}^4I_{15/2}$ transition at 70 K (upper traces) and 4.2 K (lower traces).

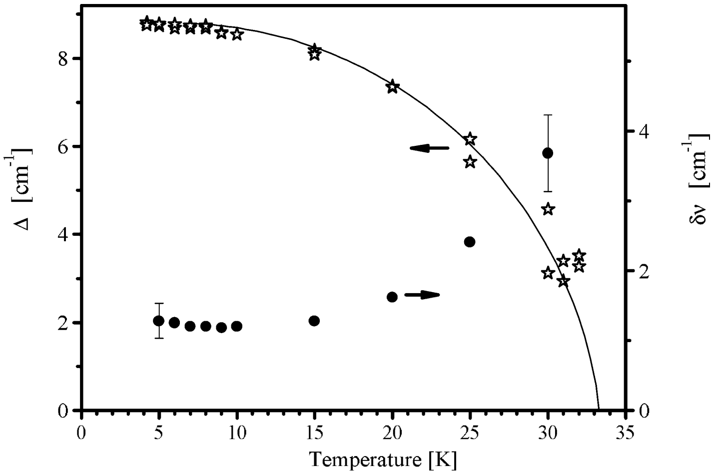

Fig. 7. Temperature dependences of the ground-state splitting Δ (stars) and the linewidth $\delta\nu$ (circles) for $NdFe_3(BO_3)_4$. A solid line is guide for the eye.

Acknowledgements

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