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Spectroscopic Study of Magnetic Phase Transitions
in $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$

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Abstract—Magnetic ordering and spin reorientation in iron borates $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ ($x = 0.01, 0.04, 0.25, 1.0$) are studied using a rare-earth spectroscopic probe. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

Owing to their physical properties and their mechanical and chemical resistance, rare-earth (RE) borates $\text{RM}_3(\text{BO}_3)_4$ ($R = \text{Y, Ln}$; $M = \text{Al, Ga, Cr, Fe, Sc}$) are promising materials for quantum- and optoelectronics. $\text{YAl}_3(\text{BO}_3)_4$ and $\text{GdAl}_3(\text{BO}_3)_4$ crystals are employed in frequency-doubled and frequency-mixed lasers, while $\text{NdAl}_3(\text{BO}_3)_4$ is a highly effective concentrated material for miniature medium-power lasers [1–3]. The compound obtained by replacing Al^{3+} with Fe^{3+} ions (which have a magnetic moment) is an interesting magnetic material containing two magnetic subsystems, namely, the RE subsystem and the iron subsystem, the latter being quasi-one-dimensional.

The compounds mentioned above crystallize in the trigonal system and belong to trigonal space group $R\bar{3}2(D_3^7)$ [4]. $\text{RFe}_3(\text{BO}_3)_4$ crystals are shaped like a hexagonal prism and consist of layers perpendicular to the c axis, which, in turn, consist of RO_6 trigonal prisms and FeO_6 octahedra (smaller in size). The RO_6 polyhedra are linked to BO_3 groups of two types and to FeO_6 octahedra by shared vertices in such a way that each FeO_6 octahedron shares two faces, one with each of the two adjacent layers. The FeO_6 octahedra share a common face with each other in such a way that they form isolated helical chains, which are parallel to the c axis and are independent of each other. The R^{3+} ions occupy equivalent positions with trigonal symmetry (point group D_3).

The magnetic properties of iron borates were measured in [4–6]. The temperature dependence of the magnetic susceptibility exhibits an anomaly at 32 K for $\text{NdFe}_3(\text{BO}_3)_4$ [4] and at 10 and 40 K for $\text{GdFe}_3(\text{BO}_3)_4$ [5, 6]. From the temperature dependence of the transmission spectra, it follows that $\text{NdFe}_3(\text{BO}_3)_4$ undergoes

magnetic ordering at 33 ± 1 K [7]. Studies of the heat capacity and Raman scattering in $\text{GdFe}_3(\text{BO}_3)_4$ and of the absorption spectra of a Nd^{3+} probe in $\text{GdFe}_3(\text{BO}_3)_4$, in combination with measurements of the magnetic properties of $\text{GdFe}_3(\text{BO}_3)_4$ [8], show that gadolinium iron borate undergoes three phase transitions: a first-order structural transition at 156 K, magnetic ordering (a second-order transition) at 37 K, and spin reorientation (a first-order transition) at 9 K [8]. In [6], the temperature dependences of the heat capacity and magnetic susceptibility of several RE iron borates were measured and the temperatures of the structural phase transition and magnetic ordering in $\text{RM}_3(\text{BO}_3)_4$ were found as a function of the R^{3+} ionic radius. In this paper, we report on the results of spectroscopic studies on magnetic phase transitions in the mixed system $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$.

2. EXPERIMENTAL

Transparent dark-green $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ ($x = 0.01, 0.04, 0.25, 1.0$) single crystals of high optical quality were grown using the flux-melt method [9]. From these prism-shaped crystals with $x = 0.01, 0.04, 0.25$, and 1.0, plates were cut with thicknesses of 0.2, 0.2, 1.0, and 0.15 mm, respectively. The samples were not oriented, and all subsequent measurements were performed in unpolarized light.

A sample was mounted on a special insert inside an optical helium-vapor cryostat. A thermocouple was located in the immediate vicinity of the sample. The temperature control system used made it possible to stabilize the temperature to within ± 0.05 K and perform measurements over the range from 4.2 to 300 K to within ± 0.05 K. The low-temperature transmission spectra of the borate single crystals under study were measured over the spectral range 5000–14000 cm^{-1}

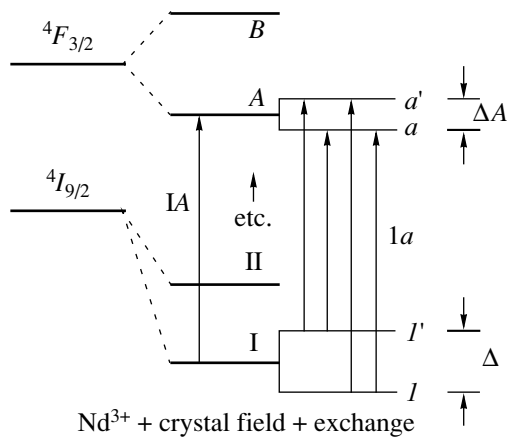


Fig. 1. Splitting of the Nd^{3+} ion levels in a D_3 -symmetry crystal field (schematic).

with a resolution of 1 to 0.15 cm^{-1} on a BOMEM DA3.002 high-resolution Fourier spectrometer equipped with a liquid-nitrogen-cooled InSb detector.

3. RESULTS AND DISCUSSION

As indicated above, the local symmetry of the RE center in iron borates is described by the D_3 point group. The Nd^{3+} ion has an odd number of electrons and is a Kramers ion. A D_3 -symmetry crystal field lifts the degeneracy of the levels of a free ion except the Kramers degeneracy. The number of levels is dictated by the value of the total angular momentum J ; a $(2J + 1)$ -fold degenerate level is split into $(J + 1/2)$ Kramers doublets. The crystal-field splitting of the Nd^{3+} ion levels is shown schematically in Fig. 1.

Figure 2 shows the transmission spectra of $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ at 50 K (in the paramagnetic phase) in the region of the transitions $4I_{9/2} \rightarrow 4I_{15/2}$ (for $x = 0.25, 1.0$) and $4I_{9/2} \rightarrow 4F_{3/2}$ (for $x = 0.01, 0.04$). With our samples, we could not study one spectral region for all values of x , because the $4I_{9/2} \rightarrow 4I_{15/2}$ transition is not observed in samples with small values of x , whereas the $4I_{9/2} \rightarrow 4F_{3/2}$ transition is saturated in samples with large values of x .

In the case where there is magnetic ordering in a sample, the RE ion is subjected to an effective magnetic field, which splits the Kramers doublets and thereby causes splitting of the spectral lines. Therefore, the optical spectra contain information on magnetic phase transitions. In iron borates, the RE ions are isolated; therefore, their interaction with one another is much weaker than the RE ion-Fe interaction and the variations in the RE spectrum are associated, for the most part, with changes in the magnetic system of Fe ions. Figure 3 shows in more detail the low-frequency lines of the transitions $4I_{9/2} \rightarrow 4I_{15/2}$ (for $x = 0.25, 1.0$) and $4I_{9/2} \rightarrow 4F_{3/2}$ (for $x = 0.01, 0.04$) at various tempera-

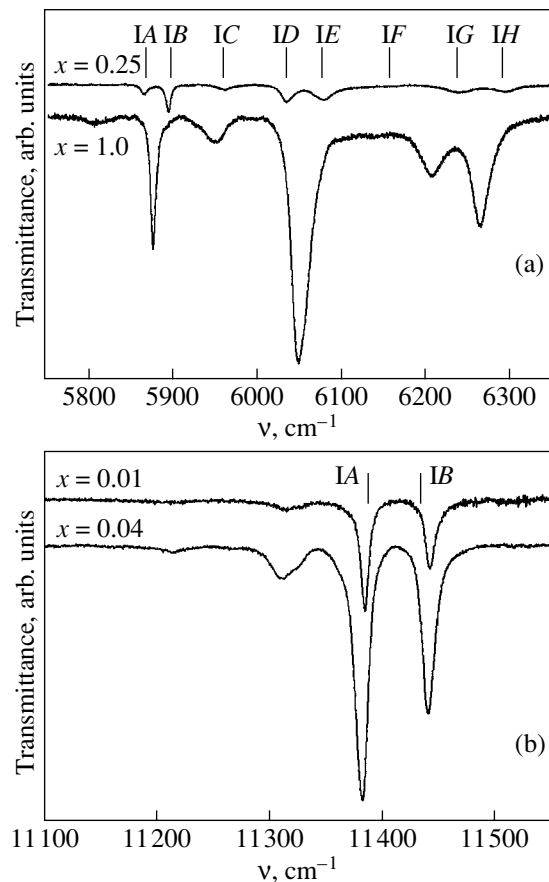


Fig. 2. Transmission spectra of $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ in the region of the transitions (a) $4I_{9/2} \rightarrow 4I_{15/2}$ (for $x = 0.25, 1.0$) and (b) $4I_{9/2} \rightarrow 4F_{3/2}$ (for $x = 0.01, 0.04$). $T = 50 \text{ K}$. The designations of the spectral lines correspond to those of the energy levels in Fig. 1.

tures. At $T > 40 \text{ K}$, the spectra are seen to have one broad line. As the temperature decreases, this line splits, because the Kramers degeneracy of the Stark levels of the Nd^{3+} ion is lifted when magnetic ordering occurs in $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$. The designations of the components of split lines in Fig. 3 correspond to those of the energy levels in Fig. 1. In the case of $\text{NdFe}_3(\text{BO}_3)_4$, splitting of the two closely spaced lines IA and IB in the spectral range $5850\text{--}5910 \text{ cm}^{-1}$ is seen to occur, as can also be clearly seen from a comparison with the spectrum of the compound with $x = 0.25$ in this spectral range (Fig. 2a). The components of these split lines corresponding to transitions from the upper sub-level of the Kramers doublet split by the magnetic interaction in the magnetically ordered state are “frozen out” at low temperatures. For the $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ compounds with $x = 0.01, 0.04$, and 0.25 , a sharp change in the relative intensity of lines is also seen to occur within a narrow temperature range (less than 1-K wide). For the earlier studied compound $\text{GdFe}_3(\text{BO}_3)_4$: Nd (1 at. %), this change in the relative intensities in the

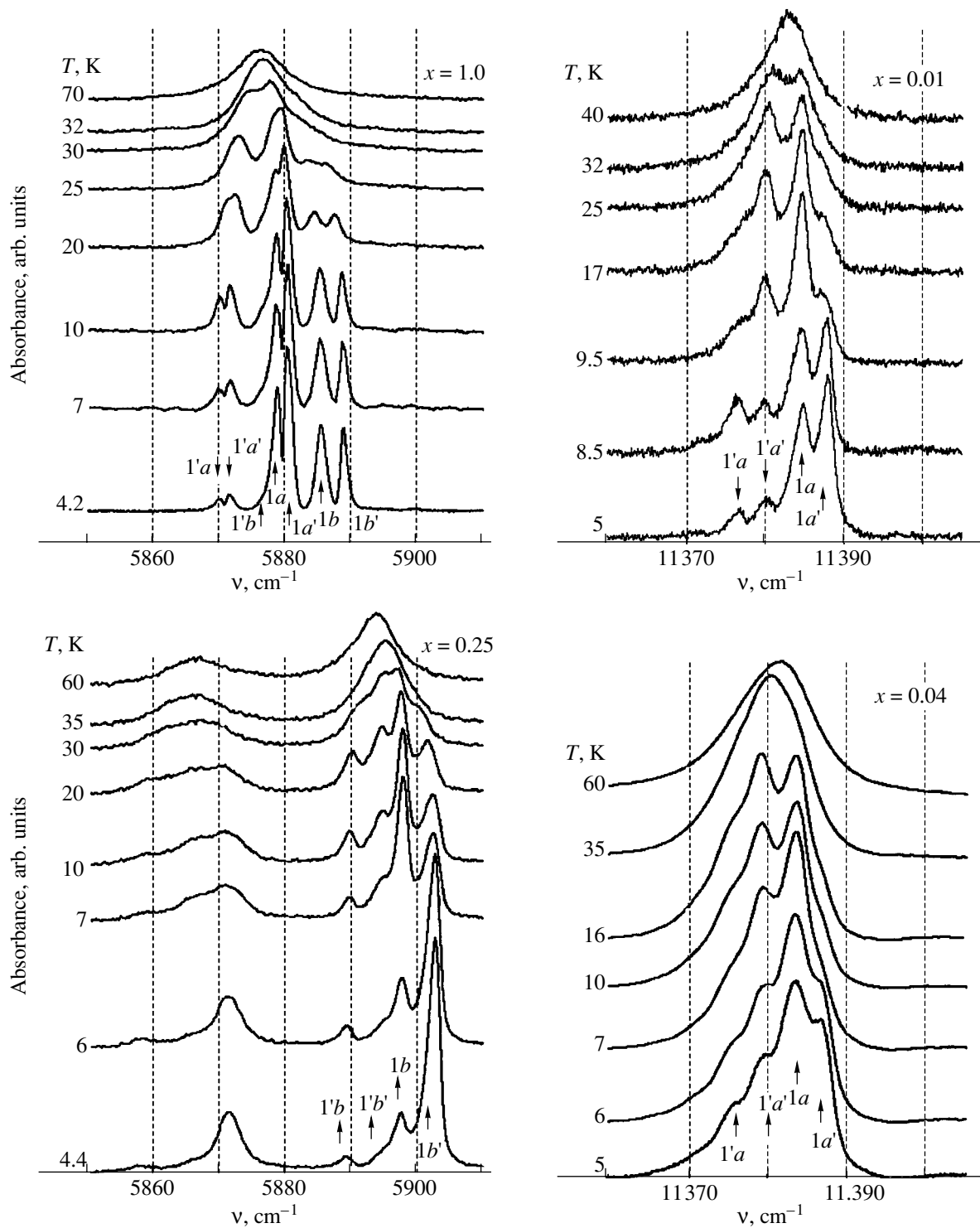


Fig. 3. Absorption spectra in the region of low-frequency lines of the transitions ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ (for $x = 0.25, 1.0$) and ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ (for $x = 0.01, 0.04$) at various temperatures.

RE spectrum (observed at $T_R = 9$ K) was assigned to the spin reorientation first-order phase transition, during which the magnetic moments of the Fe ions change their orientation from the ab plane (at temperatures T_R

$< T < T_N$) to the c axis (at $T < T_R$) [8]. The temperatures of the magnetic ordering and the spin-reorientation transition as determined from the temperature dependences of the splittings and relative intensities of the

Temperatures of magnetic ordering (T_N) and the spin-reorientation transition (T_R) in $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ as a function of x

x	T_N , K	T_R , K
0.01	37.0 ± 0.5 [8]	9.00 ± 0.25
0.04	37.0 ± 1.0	7.0 ± 0.5
0.25	36.5 ± 1.0	6.5 ± 0.5
1.0	33 ± 1 [7]	–

spectral lines are given in the table. In $\text{NdFe}_3(\text{BO}_3)_4$, the spin-reorientation transition is not observed above 3 K. The decrease in the magnetic-ordering temperature with an increase in the Nd^{3+} ion concentration in $\text{Nd}_x\text{Gd}_{1-x}\text{Fe}_3(\text{BO}_3)_4$ is due to the fact that the replacement of Gd^{3+} by Nd^{3+} (which has a larger ionic radius) increases the interatomic distances and the lattice parameters. This behavior is consistent with the variations in T_N of iron borates $\text{RFe}_3(\text{BO}_3)_4$ along the row of RE elements [6] and indicates that the links between the Fe chains are mainly due to BO_3 groups rather than to RE ions. As for the spin-reorientation transition, which is associated with temperature variations in the anisotropy of magnetic interactions [10], the available data are insufficient to explain the tendency of T_R to decrease as the neodymium content increases.

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REFERENCES

1. D. Jaque, *J. Alloys Compd.* **323–324**, 204 (2001).
2. M. Huang, Y. Chen, X. Chen, Y. Huang, and Z. Luo, *Opt. Commun.* **208**, 163 (2002).
3. X. Chen, Z. Luo, D. Jaque, J. J. Romero, J. G. Sole, Y. Huang, A. Jiang, and C. Tu, *J. Phys.: Condens. Matter* **13**, 1171 (2001).
4. J. A. Campá, C. Cascales, E. Gutierrez-Puebla, M. A. Monge, I. Rasines, and C. Ruíz-Valero, *Chem. Mater.* **9** (9), 237 (1997).
5. D. Balaev, L. N. Bezmaternyh, I. A. Gudim, V. L. Temerov, S. G. Ovchinnikov, and S. A. Kharlamova, *J. Magn. Magn. Mater.* **258–259**, 532 (2003).
6. Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima, and A. Alemi, *J. Solid State Chem.* **172**, 438 (2003).
7. E. P. Chukalina, D. Yu. Kuritsin, and M. N. Popova, *Phys. Lett. A* **322**, 239 (2004).
8. R. Z. Levitin, E. A. Popova, R. M. Chtsherbov, A. N. Vasil'ev, M. N. Popova, E. P. Chukalina, S. A. Klimin, P. H. M. van Loosdrecht, D. Fausti, and L. N. Bezmaternyh, *Pis'ma Zh. Éksp. Teor. Fiz.* **79** (9), 531 (2004) [*JETP Lett.* **79** (9), 423 (2004)].
9. L. N. Bezmaternyh, V. G. Mashchenko, N. A. Sokolova, and V. L. Temerov, *J. Cryst. Growth* **69**, 407 (1984).
10. K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and R. Z. Levitin, *Oriental Transitions in Rare-Earth Magnets* (Nauka, Moscow, 1979) [in Russian].

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