University of Groningen

Cascade of Phase Transitions in $\text{GdFe}_3(\text{BO}_3)_4$

Levitin, R.Z.; Popova, E.A.; Chtsherbov, R.M.; Vasiliev, A.N.; Popova, M.N.; Chukalina, E.P.; Klimin, S.A.; Loosdrecht, P.H.M. van; Fausti, D.; Bezmaternykh, L.N.

Published in:
Journal of Experimental and Theoretical Physics Letters

DOI:
[10.1134/1.1776236](https://doi.org/10.1134/1.1776236)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Levitin, R. Z., Popova, E. A., Chtsherbov, R. M., Vasiliev, A. N., Popova, M. N., Chukalina, E. P., Klimin, S. A., Loosdrecht, P. H. M. V., Fausti, D., & Bezmaternykh, L. N. (2004). Cascade of Phase Transitions in $\text{GdFe}_3(\text{BO}_3)_4$. *Journal of Experimental and Theoretical Physics Letters*, 79(9).
<https://doi.org/10.1134/1.1776236>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Cascade of Phase Transitions in $\text{GdFe}_3(\text{BO}_3)_4$ [†]

R. Z. Levitin^{†,1}, E. A. Popova¹, R. M. Chtsherbov¹, A. N. Vasiliev¹, M. N. Popova^{2,*},
E. P. Chukalina², S. A. Klimin^{2,3}, P. H. M. van Loosdrecht³,
D. Fausti³, and L. N. Bezmaternykh⁴

¹ Faculty of Physics, Moscow State University, Moscow, 119992 Russia

² Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142190 Russia

* e-mail: popova@isan.troitsk.ru

³ Material Science Center, University of Groningen, 9747 AG Groningen, The Netherlands

⁴ Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

Received March 29, 2004

Cascade of phase transitions in $\text{GdFe}_3(\text{BO}_3)_4$ at 156, 37, and 9 K has been detected by specific heat measurements and further studied by Raman scattering and Nd^{3+} spectroscopic probe method. A weakly first-order structural phase transition at 156 K is followed by a second-order antiferromagnetic ordering phase transition at 37 K and a first-order spin-reorientational phase transition at 9 K. © 2004 MAIK "Nauka/Interperiodica".

PACS numbers: 65.40.Ba; 71.70.Gm; 75.30.Et; 75.40.Cx; 78.30.Hv; 75.30.Kz

Borates with general formula $\text{RM}_3(\text{BO}_3)_4$, where R stands for a rare earth or yttrium and M = Al, Ga, Fe, or Sc, have attracted considerable attention because of their good luminescent and nonlinear optical properties combined with excellent physical and chemical characteristics. Crystals of $\text{YAl}_3(\text{BO}_3)_4$ and $\text{GdAl}_3(\text{BO}_3)_4$ doped with neodymium are used for self-frequency doubling and self-frequency summing lasers [1–3]. Concentrated $\text{NdAl}_3(\text{BO}_3)_4$ crystals are efficient media for minilasers [3].

Rare earth ferrobates are the least studied compounds of the $\text{RM}_3(\text{BO}_3)_4$ family. At room temperature, $\text{GdFe}_3(\text{BO}_3)_4$ crystals have the trigonal structure with the space group D_3^7 ($R\bar{3}2$ [4]). FeO_6 octahedra linked together by their edges form spiral chains running along the c axis. Gd^{3+} ions reside in D_3 symmetry positions situated between three such chains and link the chains together. GdO_6 prisms are isolated from each other, having no oxygen atoms in common. Each oxygen atom at a vertex of the GdO_6 prism belongs also to a BO_3 triangle. An indication of a structural phase transition at 174 K has been found recently by specific heat measurements on a powder sample [5].

Measurements of the magnetic properties of $\text{GdFe}_3(\text{BO}_3)_4$ were performed in [5, 6], and an anomalous behavior of magnetization was detected at about 40 and 10 K. In the present communication, we report on the temperature-dependent specific heat, Raman, and optical absorption measurements on $\text{GdFe}_3(\text{BO}_3)_4$

single crystals, pure or doped with 1 at. % of Nd introduced as a spectroscopic probe.

Crystals of $\text{GdFe}_3(\text{BO}_3)_4$ and $\text{Nd}_{0.01}\text{Gd}_{0.99}\text{Fe}_3(\text{BO}_3)_4$ were grown using a $\text{K}_2\text{Mo}_3\text{O}_{10}$ -based flux, as described in [6]. Big transparent single crystals of ferrobates were green in color and had a good optical quality. Thin plates 5–10 mm in size with different thickness (between 2.2 mm and 150 μm) were prepared for optical measurements. Specific heat in the range 5–300 K was measured by a "Termis" relaxation-type microcalorimeter. Raman measurements were made on a Jobin-Yvon T64000 spectrometer with nitrogen-cooled CCD camera in backscattering geometry. The scattering was excited by the second harmonic of a Nd:YAG laser at 532 nm, with a typical power of 10 mW. The sample was attached by silver paste to a cold finger of an Oxford Instruments helium flow cryostat "Microstat." Optical absorption spectra in the spectral region 4000–20000 cm^{-1} at a resolution of 0.2 cm^{-1} were registered by a Fourier-transform spectrometer BOMEM DA3.002 with InSb liquid nitrogen cooled detector and Si detector at sample temperatures between 4.2 and 300 K.

The temperature dependence of the specific heat of $\text{GdFe}_3(\text{BO}_3)_4$ is shown in Fig. 1. Three distinct peaks are seen in this dependence. Two of them, namely, at 9 and 156 K, are very narrow and almost symmetric, while that at 37 K is much broader and asymmetric.

The (zx) polarized Raman spectra of $\text{GdFe}_3(\text{BO}_3)_4$ are shown in Fig. 2. At about $T_c = 156$ K, several new vibrational modes appear, abruptly manifesting a structural phase transition into a less symmetric phase. The

[†] Deceased.

[†] This article was submitted by the authors in English.

Fig. 1. Specific heat of $\text{GdFe}_3(\text{BO}_3)_4$ vs. temperature.

Fig. 2. Raman spectra of $\text{GdFe}_3(\text{BO}_3)_4$ above and below the temperature of a structural phase transition $T_c = 156$ K. Inset shows the temperature dependence of the intensity of the lowest-frequency new mode when cooling (balls) and heating (stars).

Fig. 3. Temperature dependence of the frequency of the lowest new Raman mode that appears in $\text{GdFe}_3(\text{BO}_3)_4$ below $T_c = 156$ K.

small difference in T_c determined from specific heat and Raman measurements is due to a heating of the sample by light that excites Raman scattering. The inset to Fig. 2 illustrates the hysteretic temperature dependence of the intensity of the lowest-frequency new mode. All the modes shift with decreasing temperature, typically 1–2 cm^{-1} in the range of temperatures between T_c and 2.5 K. The lowest-frequency new mode demonstrates an unusually big shift. Its frequency changes from 26 cm^{-1} at T_c to 55 cm^{-1} at 2.5 K and has a peculiarity at 37 K (see Fig. 3).

To further study the observed phase transitions, we used the Nd^{3+} ion introduced as a spectroscopic probe. An energy level of the Nd^{3+} ion with the total momentum J is split into $(J + 1/2)$ Kramers doublets by a crystal field of any symmetry lower than a cubic one. Nd^{3+} substitutes for Gd^{3+} in the lattice of $\text{GdFe}_3(\text{BO}_3)_4$. The number of lines in the spectra of $\text{GdFe}_3(\text{BO}_3)_4\text{:Nd}(1\%)$ corresponds to only one position for a rare earth, both above and below the temperature 156 K of the structural phase transition. For example, for $T > 40$ K, there are two spectral lines due to the optical transitions from the ground state to the crystal-field sublevels of the $^4F_{3/2}$ level. Figure 4 shows the lowest frequency of these two lines at different temperatures. The growing splitting of the line below 37 K is due to the splitting of Nd^{3+} Kramers doublets caused by an internal magnetic field that appears at the sites of the Nd^{3+} ions in a magnetically ordered state of $\text{GdFe}_3(\text{BO}_3)_4$. Maximum four lines should appear at an optical transition between two split Kramers doublets, and these are clearly seen at low temperatures. Two low-frequency ones freeze out with a further decrease in temperature due to an emptying of the upper component of the split ground Kramers doublet of Nd^{3+} . Figure 5 displays the temperature dependence of the line splitting and of the relative intensities of two high-frequency components of the split spectral line. Sharp changes of these two quantities are observed between 9.5 and 8 K.

Each of the three phase transitions observed in $\text{GdFe}_3(\text{BO}_3)_4$ is of a different nature. A very strong narrow peak in the temperature dependence of specific heat and an abrupt appearance of new Raman modes exhibiting hysteretic behavior with a narrow hysteresis loop and a strong hardening of one mode with a further decrease in the temperature evidence a weak first-order structural phase transition at about 156 K.

Specific heat in $\text{GdFe}_3(\text{BO}_3)_4$ and Nd^{3+} spectral probe data in $\text{Nd}_{0.01}\text{Gd}_{0.99}\text{Fe}_3(\text{BO}_3)_4$ suggest a second-order magnetic ordering phase transition at about 37 K. Through the magnetoelastic interaction, the magnetic ordering also affects Raman modes and manifests itself as an aforementioned peculiarity in the shifts of these modes. Judging from the temperature dependences of magnetization given in [6], one can state that the antiferromagnetic ordering takes place at 37 K. It seems, however, that this ordering does not affect the rare earth

subsystem much, which remains paramagnetic down to lowest temperatures. In particular, this follows from the fact that the hyperbolic increase of magnetic susceptibility survives below the Neél temperature [6]. The value of magnetic entropy released at this transition, $S_{\text{magn}}^{\text{expt}} = 37 \text{ J}/(\text{mol K})$, is close to that estimated for Fe^{3+} ($s = 5/2$) subsystem ordering only ($S_{\text{magn}}^{\text{theor}} = 44 \text{ J}/(\text{mol K})$). Taking into account that the Fe^{3+} subsystem in $\text{GdFe}_3(\text{BO}_3)_4$ is of a reduced dimensionality, it is possible to assume that some part of magnetic entropy is released above the Neél temperature.

When a magnetic ordering occurs within a d -metal subsystem, the f -metal subsystem gets polarized due to the f - d exchange. For a rare earth ion, the exchange splittings and, hence, the spectral line splittings are mainly due to the exchange interactions with d ions, while the line width depends on the dipole-dipole interactions with neighboring f ions [7, 8]. In the case of Nd^{3+} probe in $\text{Nd}_{0.01}\text{Gd}_{0.99}\text{Fe}_3(\text{BO}_3)_4$, the splitting and narrowing of Nd^{3+} spectral lines manifest a magnetic ordering of the Fe subsystem and polarization of the Gd subsystem below 37 K.

At 9 K, a sharp peak in specific heat characteristic of first-order phase transition is seen. The Nd^{3+} probe spectrum changes at this temperature, showing the superposition of high-temperature and low-temperature spectra in a narrow range in the vicinity of 9 K. Such changes are typical for a first-order spin-reorientational phase transition when two different magnetic phases coexist in a narrow range of temperatures [8]. The magnetic susceptibility data [6] evidence a sharp increase of the signal at $T < 9 \text{ K}$ in a magnetic field oriented perpendicular to the c axis. At the same time, spin-flop transitions observed below 9 K in a magnetic field parallel to the c axis indicate that the antiferromagnetic sublattices in $\text{GdFe}_3(\text{BO}_3)_4$ are oriented along the c axis. Therefore, the whole of the experimental data suggest that a spin-reorientational phase transition takes place at 9 K. Above this temperature, the iron magnetic moments are oriented perpendicular to the c axis, while below this temperature, the iron moments are oriented along the c axis. In accordance with this inference, the magnetic susceptibility at $T > 9 \text{ K}$ is almost isotropic, which is typical for an easy-plane antiferromagnet.

In summary, we have registered by specific heat measurements three phase transitions (at 156, 37, and 9 K) in $\text{GdFe}_3(\text{BO}_3)_4$. We further studied these transitions by Raman and optical absorption measurements. The absorption spectra of the Nd^{3+} ion introduced as a probe into the $\text{GdFe}_3(\text{BO}_3)_4$ matrix were registered. The transition at 37 K was found to be a second-order magnetic-ordering phase transition. All the remaining transitions are first-order ones. At 156 K, the appearance of new Raman modes manifests a change of the crystal structure to a less symmetric one. The spectra of Nd^{3+} probe evidence a spin-reorientation at 9 K.

Fig. 4. Spectral line of the Nd^{3+} probe in $\text{GdFe}_3(\text{BO}_3)_4$ at different temperatures.

Fig. 5. Temperature dependences of the line splitting (balls) and relative intensities of the highest-frequency components (stars) for the Nd^{3+} probe in $\text{GdFe}_3(\text{BO}_3)_4$.

In conclusion, we are grateful to V.I. Marchenko for useful discussions. We acknowledge the support from the Russian Foundation for Basic Research (project nos. 04-02-17346, 02-02-16636, and 03-02-16286), the Russian Ministry of Science and Technology, and the Russian Academy of Sciences under the Programs for Basic Research. Part of this work was supported by the

Stichting voor Fundamenteel Onderzoek der Materie (FOM) and by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

REFERENCES

1. D. Jaque, J. Alloys Compd. **323–324**, 204 (2001).
2. M. Huang, Y. Chen, X. Chen, *et al.*, Opt. Commun. **208**, 163 (2002).
3. X. Chen, Z. Luo, D. Jaque, *et al.*, J. Phys.: Condens. Matter **13**, 1171 (2001).
4. J. A. Campa, C. Cascales, E. Gutierrez-Puebla, *et al.*, Chem. Mater. **9**, 237 (1997).
5. Y. Hinatsu, Y. Doi, K. Ito, *et al.*, J. Solid State Chem. **172**, 438 (2003).
6. D. Balaev, L. N. Bezmaternyh, I. A. Gudim, *et al.*, J. Magn. Magn. Mater. **258–259**, 532 (2003).
7. M. Baran, H. Szymczak, S. A. Klimin, *et al.*, Zh. Éksp. Teor. Fiz. **111**, 318 (1997) [JETP **84**, 175 (1997)].
8. M. N. Popova, J. Alloys Compd. **275–277**, 142 (1998).