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Studies of magnetic and optic properties of rare-earth gallo-ferroborates by Mössbauer and optical spectroscopy

O.A. Bayukov[a,*], A.M. Gavrilyuk[b], V.N. Zabluda[a], I.S. Lyubutin[c], S.G. Ovchinnikov[a], A.M. Potseluyko[a], M. Tomas[d], I.A. Trojan[b], S.A. Kharlamova[a]

[a]*LV Kirensky Institute of Physics, Siberian Branch of RAS, Krasnoyarsk, Russian Federation*
[b]*Institute of High Pressure Physics, 142190, Troisk, Moscow region, Russian Federation*
[c]*Institute of Crystallograhy, 117333, Leninsky Av. 59, Moscow, Russian Federation*
[d]*The University of Liverpool, Liverpool L69 3BX, UK*

Abstract

Magnetic and optical properties of $GdFe_{3-x}Ga_x(BO_3)_4$ single crystals are investigated by Mössbauer and optical spectroscopy. The $GdFe_3(BO_3)_4$ multielectron band structure model is derived. A high- and low-spin crossover of Fe^{3+} ion, a collapse of the magnetic moment, the suppression of Coulomb correlations, and insulator–semiconductor transition are predicted. The jump of an energy gap is measured at pressure 43 GPa.

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Keywords: Strongly correlated electron system; Antiferromagnets; Borates

1. Among strongly correlated electron system (SCES) the borates $GdFe_3(BO_3)_4$ (GFB) and $GdFe_{3-x}Ga_x(BO_3)_4$ (GFGB) from $RFe_3(BO_3)_4$ family having 3d- and 4f-electronic configurations are interesting. These crystals are antiferromagnets with Neel temperature $T_N = 38$ K (GFB) and $T_N = 15$ K (GFGB)]. Also borates are magnetic insulators, transparent in a visible range.

2. GFB Mössbauer spectra were carried out using a spectrometer with multi-channel analyzer AI-4096-3 M in the constant accelerations regime, source Co^{57} (Cr). For measurements at low temperatures (5, 20 and 40 K), a cryostat which was pumped up by liquid helium for reception of low temperature was used. ^{57}Co in matrix Rh was used as a source. Optical absorption spectra single crystals GFB were taken in a range up to 62 GPa at room temperature in the chamber with diamond anvils.

*Corresponding author.

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3. The ^{57}Fe Mössbauer spectra at $T > T_N$, (Fig. 1, at 298 and 40 K) represent an asymmetric doublet. Chemical isomeric shift relative α-Fe, $\delta = 0.39$ mm/s, $G = 0.30$ mm/s is characteristic for Fe^{3+}. The quadrupled splitting $t = 0.29$ mm/s is also typical for valence Fe^{3+} and indicates slightly deformed coordination of oxygen octahedron. At $T < T_N$ (20 and 5 K), the ^{57}Fe Mössbauer spectra show the magnetic hyperfine splitting with typical six lines. The Doppler shift of second order takes place. The angles between magnetic moments Fe and C_3-axis were estimated as 46 (at 20 K) and 22° (at 5 K), respectively. The angles of the electric field gradient (V_{zz}) and the moment of Fe were $\varphi = 63°$ at 20 K and $\varphi = 38°$ at 5 K. There is an Fe magnetic moment rotation at low temperatures from $T = 5$ up to 20 K.

4. Optical absorption spectra GFB and GFGB in comparison with $FeBO_3$ *at ambient pressure* are given in Fig. 2. It was found that absorption bands in GFB and $FeBO_3$ are similar. Gd^{3+} ion does not have its own absorption bands up to 4 eV [1], therefore bands A, B, and C are identified as Fe^{3+} ions absorption. The local structures FeO_6 in GFB and $FeBO_3$ are very close. So, bands A, B, and C observed in GFB (as well as in $FeBO_3$, Fig. 2(c)) results from d–d transitions of Fe^{3+} ion: $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$. Moreover, Fe–O and B–O distances (Table 1) in GFB and $FeBO_3$ are practically identical, this allows to conclude a similarity of electronic structures of these two crystals in energy range up to 4 eV in a vicinity of a Fermi level. Recently the multielectron band structure model of $FeBO_3$ was derived in Ref. [2]. This model was applied for GFB and so the strong electronic correlations were taken into account. The sp-hybridization of B

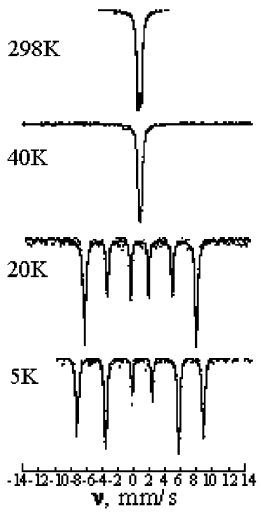

Fig. 1. Mössbauer spectra of GFB at different temperatures.

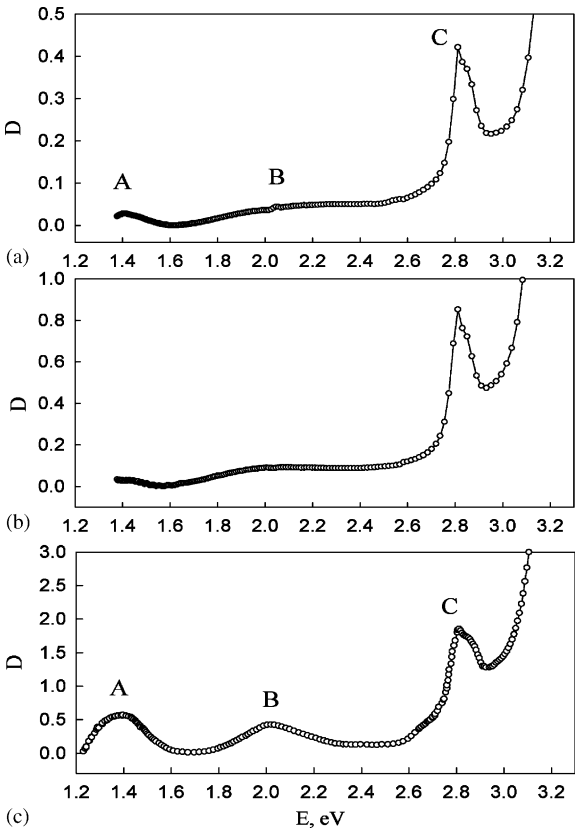

Fig. 2. Optical absorption spectra at ambient pressure: (a) $GdFe_3(BO_3)_4$ and (b) $GdFe_{2.1}Ga_{0.9}(BO_3)_4$ in comparison with (c) $FeBO_3$.

Table 1
The B–O and Fe–O distances, an energy gap (E_g) in crystals $FeBO_3$ and $GdFe_3(BO_3)_4$

	B–O (Å)	Fe–O (Å)	E_g (eV)
$FeBO_3$	1.3790	2.028	2.9
$GdFe_3(BO_3)_4$	1.3676	2.029	3.1

and O ions is very strong, d- and sp-electrons hybridization are very weak. The valence (E_v) and conductivity (E_c) bands are separated by band gap, $E_c - E_v = Eg_o = 3.1$ eV. The d-electron addition and removal states are presented by two electron levels: $\Omega_c = E(^5T_2, d^6) - E(^6A_1, d^5)$ and $\Omega_v = E(^6A_1, d^5) - E(^5E_1, d^4)$ that are equivalent to Hubbard sub-bands. The effective Hubbard parameter is $U_{eff} = \Omega_c - \Omega_v = A + 28B - \Delta = 4.2$ eV, where A, B are the Racah parameters and Δ is the crystal field, respectively.

5. Recently [3] in $FeBO_3$, a magnetic moment collapse, sharp reduction of an energy gap, and insulator–semiconductor transition under high pressure have been found. Due to the similarity in $FeBO_3$ and GFB electronic structures we can assume the same phenomena in GFB too. On increase of pressure the main change of electronic structure is induced by growth of crystal field Δ, $\Delta(P) = \Delta(0) + \alpha P$. The high-spin $^6A_1(S = \frac{5}{2})$ and low-spin $^2T_2(S = \frac{1}{2})$ terms of Fe^{3+} crossover takes place at $P = P_c$ resulting in the magnetic moment collapse. In a high-pressure phase, the energies of upper and lower Hubbard bands vary, and the effective parameter of Hubbard correlations changes to: $U_{eff} = A + 9B - 7C \approx 1.45$ eV. Thus, the sharp SEC reduction occurs, and we have GFB as a semiconductor (Fig. 3b). Experimentally, we have found the electronic transition in GFB at 43 GPa.

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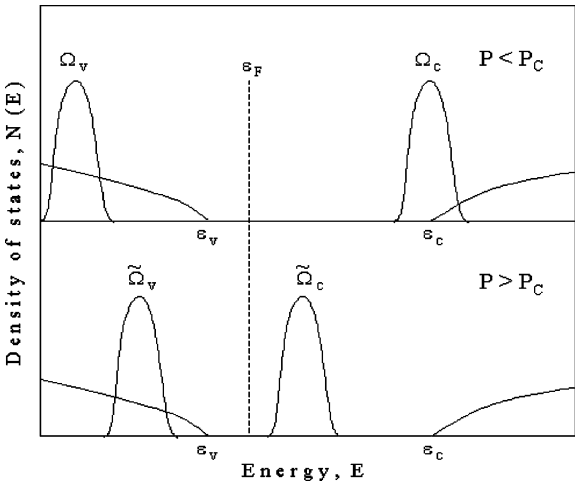

Fig. 3. Density of states of $GdFe_3(BO_3)_4$ in phases: (a) ambient and (b) high pressure.

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