Optical transitions in $GdFe_3(BO_3)_4$ and $FeBO_3$ under high pressures[*]

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Optical transitions in $GdFe_3(BO_3)_4$ and $FeBO_3$ under high pressures*

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Abstract

The optical properties of $GdFe_3(BO_3)_4$ under high pressures have been investigated experimentally and theoretically, and the results are compared with the properties of $FeBO_3$. A model of the $GdFe_3(BO_3)_4$ band structure is derived within the multielectron model taking into account the strong electron correlations. Crossover of the Fe^{3+} ion high-spin and low-spin states, collapse of the magnetic moment, the relaxation Coulomb correlations, and insulator–semiconductor transition are predicted. Optical transitions in $GdFe_3(BO_3)_4$ and $FeBO_3$ under high pressures were discovered.

1. Introduction

$GdFe_3(BO_3)_4$ (GFB), having both 3d- and 4f-transition elements, is a rare magnetic material that is transparent in the visible range. The crystal lattice has the rhombohedral (trigonal) symmetry of huntite type with space group $R\bar{3}2(D_{3h}^7)$ and with lattice parameters $a = 9.5491(6)$ Å and $c = 7.5741(5)$ Å. The iron ions Fe^{3+} are in oxygen octahedra, and the gadolinium ions Gd^{3+} are in oxygen prisms. The material is antiferromagnetic with a Néel temperature of $T_N = 38$ K [1].

$FeBO_3$ (FB) is a well known material that is transparent in the visible range and has spontaneous magnetization at room temperature. It is known that the crystal lattice of FB has rhombohedral symmetry of calcite type with space group $R\bar{3}c(D_{3d}^6)$ and with lattice parameters $a = 4.612$ Å and $c = 14.47$ Å. The iron ions Fe^{3+} are in oxygen octahedra, and interionic distances are (Fe–O) = 2.028 Å and (Fe–Fe) = 3.601 Å, while the angles of the bonds

(O–Fe–O) are 91.82° and 88.18°. Thus, the oxygen surrounding of Fe is almost cubic. At ambient conditions FB is an easy-plane antiferromagnet with weak ferromagnetism and with $T_N = 348$ K [2].

In the present work the optical properties of GFB are investigated experimentally at ambient and high pressures and the results are compared with those of FB. The multielectron model of the GFB band structure is derived taking into account the strong electron correlations. Predictions of the model are confirmed by the jump of an energy gap observed in GFB at a pressure of 43 GPa.

2. Experimental details

Single crystals of GFB and FB have been grown by a flux method. Both grown single crystals had green colour, and are transparent in the visible range. For optical measurements at ambient pressure, thin planar samples (plates) were cut from bulk isometric crystals parallel and perpendicular to the C_3 crystallographic axis. The thicknesses of the plates were $\sim$53 μm and $\sim$42 (37) μm; the area in both samples was $\sim$2 mm^2. At room temperature, optical absorption spectra $D = \text{Ln}(I_0/I)$ for GFB and FB were obtained in using a two-beam spectrometer in the range 10 000–40 000 cm^{-1} (1.24–4.96 eV). The spectral slot width of the lattice monochromator was 10 cm^{-1}. The accuracy of absorption measurements was 3%.

High-pressure optical absorption spectra were measured for a GdFe$_3$(BO$_3$)$_4$ crystal at pressures up to 60 GPa at room temperature in a diamond-anvil cell. Diamond anvils of flat diameter $\sim$400 μm were used. The hole in the centre of the rhenium gasket had a diameter of $\sim$120 μm. Measurements were performed with a thin plate of size $\sim$50 × 40 × 15 μm^3 obtained from a massive GdFe$_3$(BO$_3$)$_4$ single crystal. The light beam was directed perpendicular to the basis plane of the crystal. Pressure was applied to the sample through a PES-5 liquid providing quasihydrostatic compression. The single crystal remained undamaged after the removal of pressure. The optical setup for the study of the absorption spectra allows one to perform measurements in the visible and near-IR ranges from 0.3 to 5 μm. The light-spot diameter on the sample was $\sim$20 μm. The absorption spectrum was calculated from the expression $I = I_0 \exp(-\alpha d)$, where d is the sample thickness, I is the reference signal intensity outside the sample, and α is the absorption coefficient.

3. Results and discussion

Optical spectra at ambient pressure

The optical absorption spectra of GFB and FB at ambient pressure are given in figure 1. It was found that the absorption bands in GFB and FB are similar. The Gd^{3+} ion has no absorption bands of its own up to 4 eV [3], therefore bands **A**, **B**, **C** are identified as Fe^{3+} ion absorption bands. The local structures of FeO$_6$ octahedra in GFB and FB are very similar. So, bands **A**, **B** and **C** observed in GFB, as well as in FB (figure 1(b)), result from d–d transitions of Fe^{3+} ion: $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4A_{1g}^4, E_g$. Moreover, Fe–O and B–O distances (table 1) in GFB and FB are practically identical, and this allows us to suggest that in the vicinity of the Fermi level the electronic structures of these two crystals are similar in the energy range up to 4 eV.

The multielectron band structure model of FeBO$_3$ was derived in [4]. Here, we apply similar ideas to the GFB crystal thus taking into account the strong electronic correlations.

It was established [5], that the sp-hybridization of B and O ions is very strong whereas the d- and sp-electrons hybridization is very weak. The valence (E_v) and conductivity (E_c) bands are separated by a band gap, $E_c - E_v = E_{go} = 3.1$ eV. The great intensity of
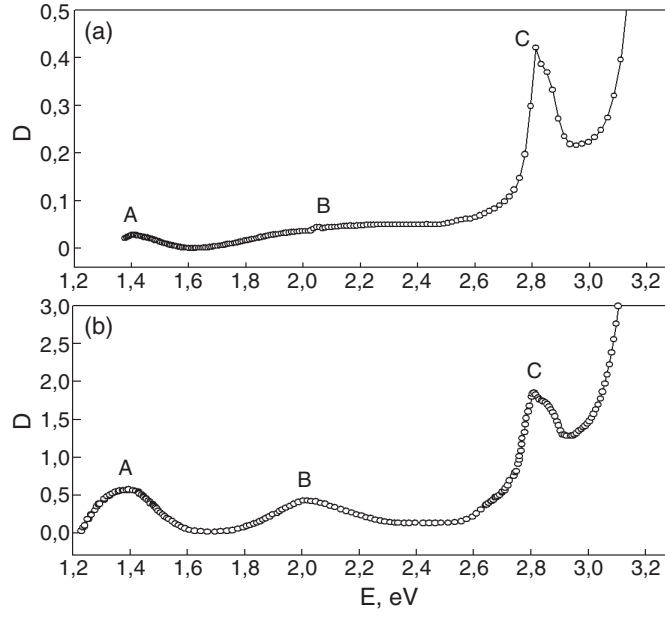
Figure 1. Optical absorption spectra at ambient conditions: (a) GdFe$_3$(BO$_3$)$_4$, (b) FeBO$_3$. The thickness of the GdFe$_3$(BO$_3$)$_4$ sample is 53 μm, and that of the FeBO$_3$ sample is 42 μm.

Table 1. B–O and Fe–O distances, and the energy gap in 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

the absorption band **C** in the spectrum of GdFe$_3$(BO$_3$)$_4$, as in the case of FeBO$_3$, can be explained by the overlap of the charge-transfer absorption due to the p^{6}d^5 → p^{5}d^6 process. The creation of an additional electron in the Fe^{3+} → Fe^{2+} transition requires the energy $\Omega_c = E(^5T_2, d^6) - E(^6A_1, d^5)$, while the annihilation of an electron (creation of a hole) requires $\Omega_v = E(^6A_1, d^5) - E(^5E_1, d^4)$, which are equivalent to Hubbard sub-bands. These levels can be presented by Racah parameters as

$$\Omega_c = \varepsilon_d + 5A + 14B - 0.4\Delta$$

and

$$\Omega_v = \varepsilon_d + 4A - 14B + 0.6\Delta.$$

The electron structure of GdFe$_3$(BO$_3$)$_4$ at ambient pressure is shown in figure 2(a). The effective Hubbard parameter is

$$U_{eff} = \Omega_c - \Omega_v = A + 28A - \Delta = 4.2 \text{ eV},$$

where A, B are the Racah parameters and Δ is the crystal field. Such a value of U_{eff} is typical for d-ions of the middle 3d-row.

Theory of optical spectra at high pressure

Recently [6–8] a magnetic moment collapse, sharp reduction of the energy gap, and an insulator–semiconductor transition has been found under high pressure in FB. Due to the
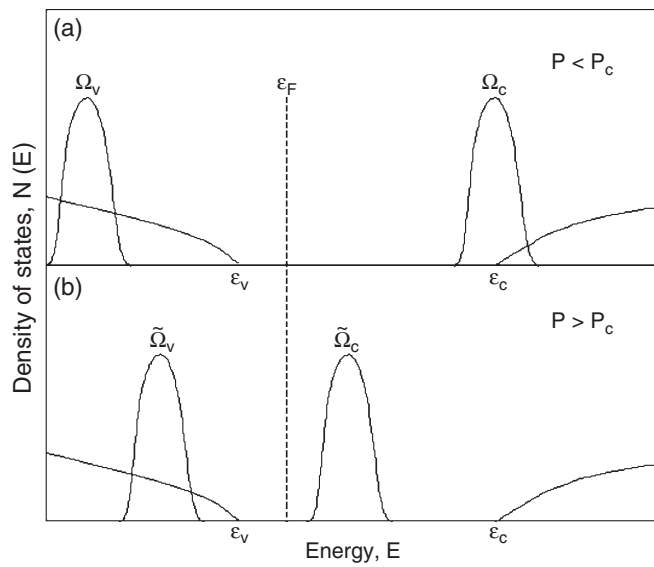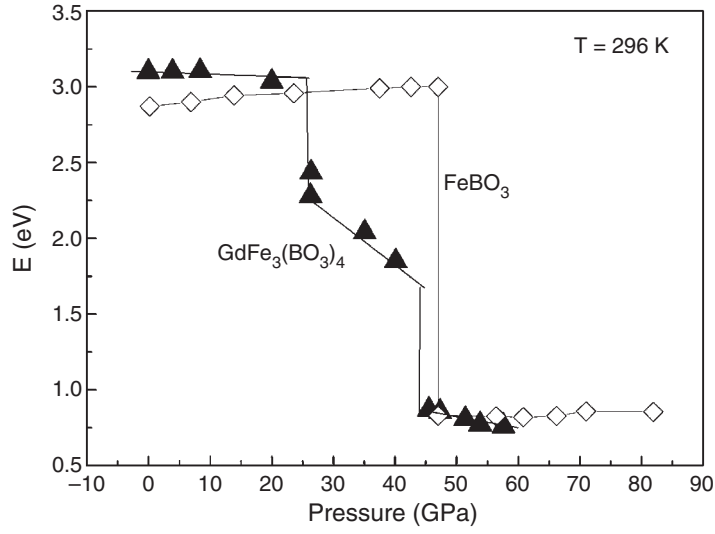
Figure 2. Electron structure of GdFe$_3$(BO$_3$)$_4$ at (a) ambient pressure, (b) high pressure.
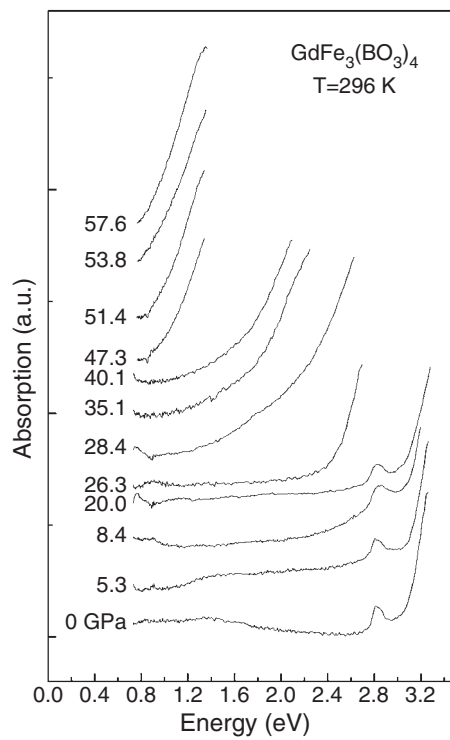
Figure 3. Optical absorption spectra of GdFe$_3$(BO$_3$)$_4$ at high pressure.

similarity of the FB and GFB electronic structures we assume the same phenomena in GFB too. With increase of pressure the main change of electronic structure is induced by growth

Figure 4. Dependence of the energy gap on pressure in GdFe$_3$(BO$_3$)$_4$ and FeBO$_3$.

of the crystal field Δ: $\Delta(P) = \Delta(0) + \alpha$. The high-spin ^{6}A$_1$ ($S = 5/2$) and low-spin ^{2}T$_2$ ($S = 1/2$) terms of the Fe^{3+} crossover take place at $P = P_c$, resulting in the magnetic moment collapse. In the high-pressure phase, the energies of the upper and lower Hubbard bands vary, and for Fe^{3+} we have

$$\Omega_c = E(^1A_1, d^6) - E(^2T_2, d^5)$$

and

$$\Omega_v = E(^2T_2, d^5) - E(^3T_1, d^4).$$

Then the effective parameter of the Hubbard correlations reduces to $U_{eff} = A + 9B - 7C \approx$ 1.45 eV. Thus, a sharp strong electron correlation reduction occurs, and in the high-pressure phase the GFB crystal is a semiconductor (figure 2(b)). Further increase in pressure results in an increase of the d-band width, which can lead to closing of the semiconducting gap with translation to a metallic state.

Experimental optical spectra at high pressure

To verify our theoretical predictions, the experimental optical absorption spectra of GFB were studied at high pressures (figure 3). Experimental details are described in section 2 of this paper. The spectrum at ambient pressure was measured with the sample inside the diamond-anvil cell and it is therefore different from the spectrum in figure 1.

The pressure dependences of the optical absorption edge in GFB (triangles) and FB (circles) [8] are shown in figure 4. The absorption edge energies were estimated as the onset of significant absorption increase (to the power of about 4–5 in log scale).

Electronic phase transitions with two sharp jumps of the energy gap (at 26 and 43 GPa) were found in GFB (figure 4), whereas only one transition takes place in FB (from [8]). At $P > 43$ GPa, in the high-pressure phase the optical gap is about 0.8 eV in both crystals. This indicates that the crystals are in a semiconducting state. A full account of this study will be published elsewhere.

Acknowledgments

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