

# The Mechanism of Suppression of Strong Electron Correlations in $\text{FeBO}_3$ at High Pressures

A. G. Gavriiliuk<sup>a,b</sup>, I. A. Trojan<sup>b</sup>, S. G. Ovchinnikov<sup>c</sup>,  
I. S. Lyubutin<sup>a</sup>, and V. A. Sarkisyan<sup>a</sup>

<sup>a</sup>Shubnikov Institute of Crystallography, Russian Academy of Sciences,  
Leninskii pr. 59, Moscow, 119333 Russia

<sup>b</sup>Institute of High-Pressure Physics, Russian Academy of Sciences,  
Troitsk, Moscow region, 142092 Russia

<sup>c</sup>Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Krasnoyarsk, 660036 Russia

e-mail: lyubutin@ns.crys.ras.ru

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**Abstract**—The optical absorption spectra of iron borate ( $\text{FeBO}_3$ ) are measured at high pressures up to  $P = 82$  GPa. A mechanism of suppression of strong electron correlations is proposed within the framework of the generalized tight binding method, which leads to the experimentally observed magnetic, electronic, and structural phase transitions. Taking into account peculiarities of the crystal structure of  $\text{FeBO}_3$  and the strong  $s$ - $p$  hybridization of boron and oxygen, it is established that, as the distance between ions varies with increasing pressure, the crystal field parameter begins to play a decisive role in the electron transitions, while the influence of the  $d$  band broadening is negligibly small. Parameters of the theory are calculated as functions of the pressure. © 2004 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

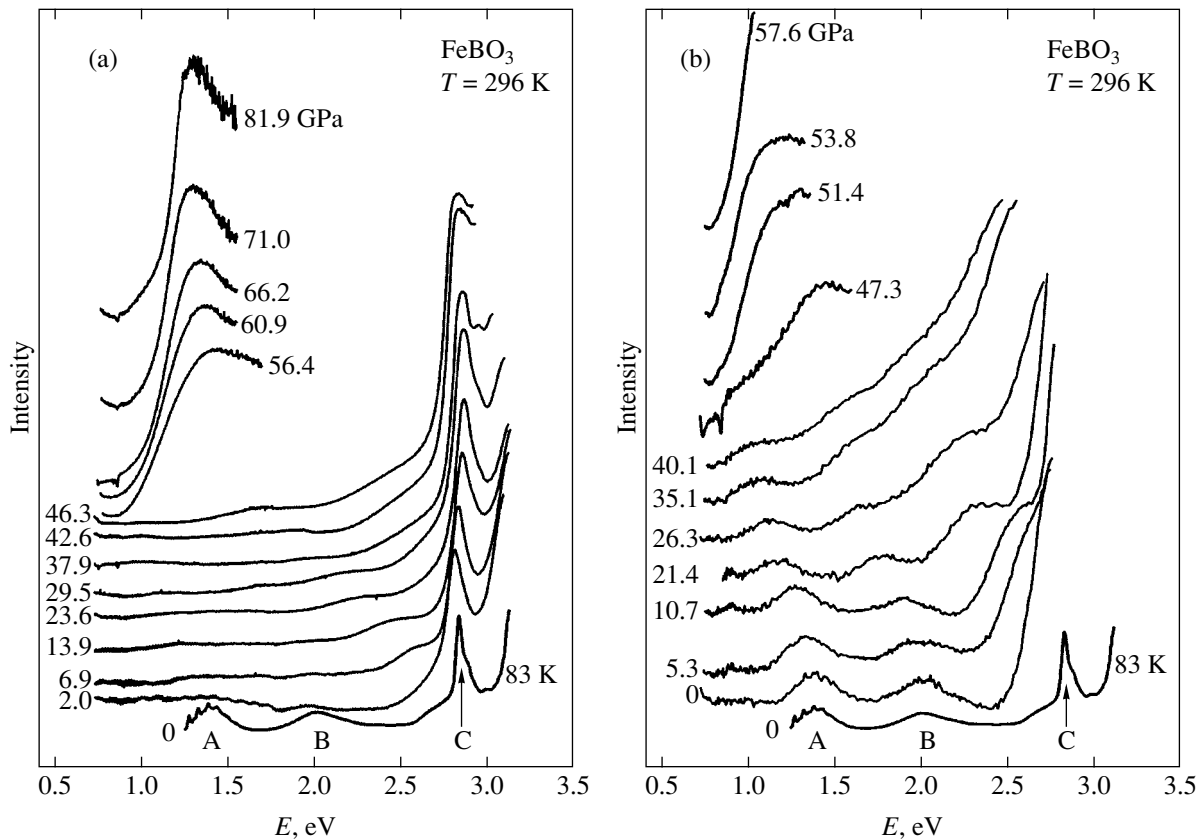
Recently [1–4], we have reported on a number of phase transitions induced by high pressure in iron borate ( $\text{FeBO}_3$ ). In particular, it was established that a transition of the magnet–nonmagnet type with collapse of the localized magnetic moment takes place at a pressure of about 47 GPa [1, 2]. An insulator–semiconductor type transition is observed at approximately the same pressure [3], and a structural phase transition with symmetry conservation ( $R\bar{3}c \rightarrow R\bar{3}c$ ) and a 9% jump in the unit cell volume takes place at about 53 GPa [4]. A model describing the electron structure of  $\text{FeBO}_3$  and its variation at high pressures [5] was developed within the framework of the generalized tight binding method for systems with strong electron correlations. However, several experimentally observed effects and some principal questions concerning the physical nature of phase transitions still remain unclear. These questions are related to factors leading to the magnetic collapse and to the fact that the electron system exhibits the transition to a semiconducting state rather than to the metallic state. It is also unclear why the magnetic and electronic transitions occur at the same pressure, while the structural transition takes place at a different pressure.

In this paper, we report on the results of experimental investigation of the optical absorption spectra of single crystal  $\text{FeBO}_3$  in a range of pressures up to 82 GPa. The dependences of the absorption spectra and the elec-

tron structure of  $\text{FeBO}_3$  on the pressure have been theoretically studied in both low- and high-pressure phases. The theory employs the generalized tight binding method for a multiband  $p$ - $d$  model [5] and combines the concepts of quasi-particles from the Landau theory of a Fermi liquid with Hubbard’s notions of the predominant role of intraatomic Coulomb interactions in systems with strong electron correlations. Parameters of the theory calculated using the experimental data are consistent with the results of observations. The proposed theory qualitatively explains many of the effects experimentally observed in  $\text{FeBO}_3$  crystals—in particular, the transition to a semiconducting (rather than metallic) state—and predicts a transition to the metallic state with further increase in pressure.

## 2. EXPERIMENTAL

High-quality, optically transparent  $\text{FeBO}_3$  single crystals of light-green color were grown from by the flux method. The optical absorption spectra were measured at room temperature in a range of pressures up to 82 GPa in a cell with diamond anvils. The diamond anvil culets were about 400  $\mu\text{m}$  in diameter, and a hole at the center of a rhenium gasket had a diameter of  $\sim 120$   $\mu\text{m}$ . The measurements were performed on  $\sim 50 \times 50$   $\mu\text{m}^2$  plates of various thicknesses from  $\sim 2$  to  $\sim 15$   $\mu\text{m}$ . The plates were cut from a massive  $\text{FeBO}_3$  single crystal so that their large faces coincided with the (111) basal plane.



**Fig. 1.** Evolution of the room-temperature absorption spectra (A, B, C are absorption bands) measured at various pressures for (a) thin ( $d = 2\text{--}3\ \mu\text{m}$ ) and (b) thick ( $d = 10\text{--}15\ \mu\text{m}$ ) single crystal  $\text{FeBO}_3$  samples (figures at the curves indicate pressure in GPa; the bottom curve shows the spectrum measured at 83 K [6]).

During the spectral measurements, the light beam in the high-pressure cell was directed perpendicular to the basal plane of the crystal and focused into a 20- $\mu\text{m}$ -diameter spot on the sample surface. Polyethyl siloxane (PES-5) was used as a pressure-transmitting medium providing quasi-hydrostatic conditions. After pressure release, the single crystal samples remained intact.

The absorption spectra at high pressure were measured in the visible and near-IR regions in the wavelength range from 0.3 to 5  $\mu\text{m}$ . The optical setup and the experimental procedure were described in detail elsewhere [3]. The absorption spectrum was calculated by the standard method using the formula

$$I = I_0 \exp(-\alpha d),$$

where  $I_0$  is the reference beam intensity,  $d$  is the sample thickness, and  $\alpha$  is the optical absorption coefficient.

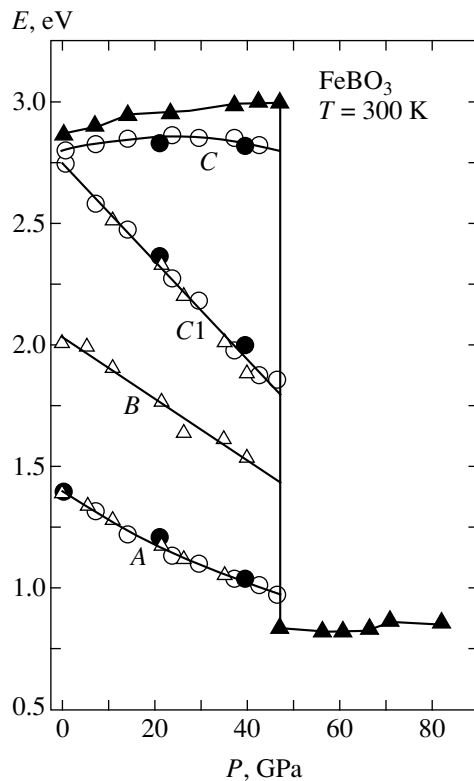
### 3. EXPERIMENTAL RESULTS: EFFECT OF PRESSURE ON THE POSITIONS OF OPTICAL ABSORPTION BANDS

Figure 1a shows evolution of the optical absorption spectra of single crystal  $\text{FeBO}_3$  with increasing pres-

sure  $P$  at room temperature. These measurements were performed on samples with a thickness of 2–3  $\mu\text{m}$ . As the pressure grows to 46 GPa, the energy of the optical absorption edge slowly increases. At  $P \approx 46$  GPa, the absorption edge energy drops abruptly from  $\sim 3$  to  $\sim 0.8$  eV and then virtually does not change as the pressure is further increased up to 82 GPa (Fig. 2). The jump in the optical gap at 46 GPa correlates with the magnetic moment collapse observed previously [1, 2] at the same pressure.

The room-temperature spectra of “thick” samples ( $d = 10\text{--}15\ \mu\text{m}$ ) also clearly reveal the evolution of the absorption bands related to various excitation processes in the electron system of  $\text{FeBO}_3$  (Fig. 1b). The positions of maxima of the absorption bands denoted by capital letters A, B and C at a zero applied pressure correspond to the energies  $1.395 \pm 0.006$ ,  $2.029 \pm 0.022$ , and  $2.803 \pm 0.005$  eV, respectively. For the comparison, Fig. 1 also shows the absorption spectrum of  $\text{FeBO}_3$  measured at 83 K [6].

According to our experimental results, band C exhibits splitting into two signals (C and C1) with increasing pressure. The absorption band C has the shape of a narrow peak (Fig. 1a) and its position can be



**Fig. 2.** Plots of the energy positions of the optical absorption edge and absorption peaks A, B, C, and C1 versus pressure for single crystal FeBO<sub>3</sub> measured at room temperature in several series of experiments (different symbols refer to samples of various thicknesses).

determined with a much better accuracy than positions of the other absorption bands. The energy of peak C weakly varies with increasing pressure as described by a quadratic law and exhibits a maximum in the region of 25 GPa.

Figure 2 shows the pressure dependence of the positions of various absorption bands and the optical absorption edge. Parameters of the electron transitions corresponding to these bands are given in the table. These parameters and related errors were calculated from experimental data using a linear approximation. For bands A and C, the experimental data were approximated using a second-degree polynomial.

The energies  $E_0$  of optical transitions at zero applied pressure and their baric derivatives at high pressures in single crystal FeBO<sub>3</sub> at room temperature. The last column presents theoretical  $dE/dP$  values (see Section 5)

Optical transition	$E_0$ , eV	$dE/dP$ , eV/GPa	$d^2E/dP^2$ , eV/(GPa) <sup>2</sup>	$(dE/dP)_{\text{theor}}$ , eV/GPa
A	$1.395 \pm 0.006$	$-0.0115 \pm 0.0007$	$(5.69 \pm 1.56) \times 10^{-5}$	-0.0156
B	$2.029 \pm 0.022$	$-0.0125 \pm 0.0009$	-	-0.0158
C	$2.803 \pm 0.005$	$+0.0051 \pm 0.0006$	$(-1.02 \pm 0.13) \times 10^{-4}$	0
C1	$2.749 \pm 0.017$	$-0.0199 \pm 0.0006$	-	-0.0174

#### 4. ELECTRON STRUCTURE OF FeBO<sub>3</sub> AND ITS PRESSURE DEPENDENCE IN MANY-ELECTRON MODEL

In the absence of applied pressure, the optical absorption spectrum of FeBO<sub>3</sub> exhibits three main bands (A, B, and C) occurring below 2.9 eV inside the bandgap. According to the traditional interpretation, these bands are due to the following exciton transitions in the  $d^5$  configuration [7–10]:

$$\omega_A = E(^4T_1) - E(^6A_1),$$

$$\omega_B = E(^4T_2) - E(^6A_1), \quad (1)$$

$$\omega_C = E(^4A_1) - E(^6A_1).$$

However, the temperature dependences of the energies of bands A, B, and C, as well as the circular dichroism spectra [11, 12], are significantly different. This poses questions concerning adequacy of the aforementioned interpretation. In particular, the intensity of peak C is much greater than the intensities of bands A and B, which suggests that an additional allowed optical transition may exist in the vicinity of  $\omega_C$ . Such a transition can be related to the electron excitation with charge transfer  $p^6d^5 \rightarrow p^5d^6$ . Both  $d-d$  excitations from the ground state to the upper  $d^5$  terms and the  $d^5 \rightarrow d^6$  transitions in many-electron  $d^n$  configurations take place under conditions of strong electron correlations. These effects cannot be adequately described using one-electron methods of the band theory.

Recently [5], a many-electron model of the electron structure of FeBO<sub>3</sub> has been developed with allowance for strong electron correlations. The absorption spectrum calculated within the framework of this model exhibits additional excitations with charge transfer [6]. The model has been described in detail in [6], but the effect of pressure on the electron structure was not considered. For this reason, we present a brief outline of this model and consider the pressure-induced changes in the electron structure of FeBO<sub>3</sub>.

The model is based on *ab initio* one-electron band calculations of the electron structure of FeBO<sub>3</sub> using the density functional method in the local spin density approximation [13] and on calculations of the molecu-

lar orbitals of a  $\text{FeB}_6\text{O}_6$  cluster [14]. Both these calculations revealed a very strong  $s$ - $p$  hybridization inside the  $\text{BO}_3$  group. The top of the filled valence band ( $\epsilon_v$ ) is formed predominantly by the  $s$ - and  $p$  states of oxygen, while the bottom of the empty conduction band ( $\epsilon_c$ ) is formed primarily by the  $s$ - and  $p$  states of boron. The bandgap  $E_{g0} = \epsilon_c - \epsilon_v$  was estimated at 2.5 eV [13], which is close to the optical absorption edge (2.9 eV [9]). According to the band calculation, the  $d$  band occurs near the top of the valence band and is partly filled, which corresponds to the metallic state. This drawback of the band theory is related to underestimation of the role of strong electron correlations.

The existing *ab initio* methods do not allow the effects of strong electron correlations to be adequately described. For this reason, we have calculated the structure of  $d$  bands using the generalized tight binding method [15], in which the addition of electron is related to  $d^5 \rightarrow d^6$  excitation. The energies of  $d^4$ ,  $d^5$ , and  $d^6$  terms are calculated taking into account strong intra-atomic Coulomb interactions and are expressed in terms of the Racah parameters  $A$ ,  $B$ ,  $C$  and the crystal field parameter  $\Delta$  determined as a difference of the energies of  $d$  levels ( $t_{2g}$  and  $e_g$ ) in the cubic environment. The energies of the lower terms (corresponding to the high-spin states at normal pressure) are

$$E_0(d^4) \equiv E(^5E, d^4) = 4\epsilon_d + 6A_4 - 21B_4 - 0.6\Delta_4,$$

$$E_0(d^5) \equiv E(^6A_1, d^5) = 5\epsilon_d + 10A_5 - 35B_5, \quad (2)$$

$$E_0(d^6) \equiv E(^5T_2, d^6) = 6\epsilon_d + 15A_6 - 21B_6 - 0.4\Delta_6,$$

where  $\epsilon_d$  is the energy of  $d$  electrons in a given atom in the one-electron approximation. In the general case, the Racah parameters corresponding to different  $n$  can vary within approximately 10%. Since our aim here is to understand qualitatively the nature of pressure-induced changes in the spectra and the electron structure, this variation of the Racah parameters can be ignored. The energy of electron addition (analogous to the upper Hubbard band) is

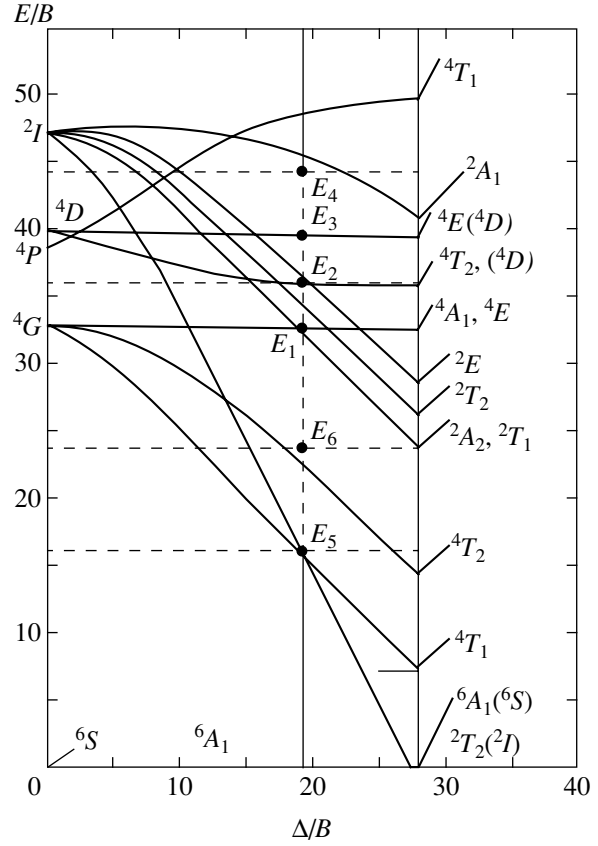
$$\Omega_c = E_0(d^6) - E_0(d^5) = \epsilon_d + 5A + 14B - 0.4\Delta, \quad (3)$$

and the energy of electron annihilation (or hole creation) is

$$\Omega_v = E_0(d^5) - E_0(d^4) = \epsilon_d + 4A - 14B + 0.6\Delta. \quad (4)$$

The Mott–Hubbard gap  $\Omega_c - \Omega_v \propto U_{\text{eff}} = A + 28B - \Delta$  has the meaning of an effective Coulomb parameter determining the magnitude of strong electron correlations.

In this theory, the parameters are  $A$ ,  $B$ ,  $C$ ,  $\Delta$ , and  $\epsilon_d - \epsilon_v$ . The values of  $B = 0.084$ ,  $C = 0.39$ ,  $\Delta = 1.57$  eV were determined from the optical absorption spectra [6, 7]

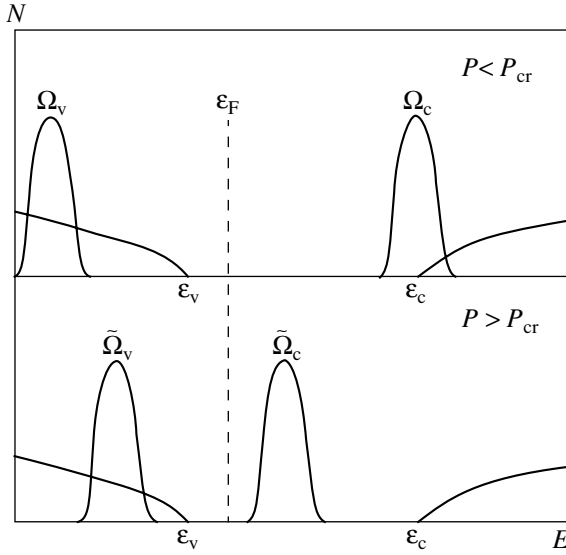


**Fig. 3.** Tanabe–Sugano diagrams for  $\text{Fe}^{3+}$  ion. Solid curves show various terms versus the crystal field parameter; dashed lines correspond to the set of parameters  $B$ ,  $C$ , and  $\Delta$  for single crystal  $\text{FeBO}_3$ .

with the aid of the Tanabe–Sugano diagram [16]. As can be seen from Fig. 3, the exciton transition energies (corresponding to peaks A, B, and C in the experimental spectrum) for these parameters are  $\omega_A = 1.39$  eV,  $\omega_B = 2.03$  eV, and  $\omega_C = 2.80$  eV. The Racah parameter  $A$  was determined in [6] from the conditions of coincidence of the energy of excitation with charge transfer  $\Omega_c - \epsilon_v$  with the energy of peak C:  $\Omega_c - \epsilon_v = \omega_C$ ; the parameter  $\epsilon_d - \epsilon_v$  was found from the conditions of coincidence of the energy  $\Omega_v - \epsilon_v$  with the energy of the  $d$  peak in the X-ray spectrum:  $\Omega_v - \epsilon_v = -1.4$  eV [13]. These conditions yield  $A = 3.42$  eV and  $\epsilon_d - \epsilon_v = -14.84$  eV. In what follows, the one-particle energies are measured from the top of the valence band of oxygen states (i.e.,  $\epsilon_v = 0$ ), so that  $\epsilon_d = -14.84$  eV.

Thus, at normal pressure,  $U_{\text{eff}} = 4.2$  eV and the electron structure of  $\text{FeBO}_3$  is characteristic of a charge transfer insulator (see the diagram for  $P < P_{\text{cr}}$  in Fig. 4).

Other parameters in the theory under consideration is the interatomic hopping parameter  $t$ , determining the  $d$ -band halfwidth  $W = Zt$  (where  $Z = 6$  is the number of nearest neighbors), and the integral of the Fe–Fe exchange interaction  $J = 2t^2/U_{\text{eff}}$ . The latter quantity, in



**Fig. 4.** Density of states in low- and high-pressure phases of single crystal FeBO<sub>3</sub> according to the many-electron  $p$ - $d$  model.

turn, determines the Néel temperature in the mean field approximation:  $T_N = ZJS(S+1)/3$ . Using these relations and the experimental value of  $T_N = 348$  K, we obtain (for  $S = 5/2$ )  $t(P=0) \equiv t_0 = 0.076$  eV. The interatomic  $d$ - $d$  hopping smears the contributions due to atomlike states (3) and (4) to the total density of states (Fig. 4), so that these contributions change from  $\delta$ -like to narrow  $d$  bands.

Now let us consider the pressure-induced changes in the electron structure of FeBO<sub>3</sub>. The intraatomic Racah parameters  $A$ ,  $B$ , and  $C$  can be considered independent of the pressure, whereas the quantities  $\Delta$ ,  $t$ , and  $E_{g0} = \epsilon_c - \epsilon_v$  may depend on the interatomic distances. In view of tight binding inside the BO<sub>3</sub> group, we assume that this group is rigid (i.e., insignificantly deformed by increasing pressure). Then, the energy of the top of the valence band and the bandgap  $E_{g0}$  between the conduction and valence bands can be considered constant. Assuming also that the parameters  $t$  and  $\Delta$  linearly increase with the pressure,

$$\begin{aligned} t(P) &= t_0 + \alpha_t P, \\ \Delta(P) &= \Delta_0 + \alpha_\Delta P, \end{aligned} \quad (5)$$

we infer that  $U_{\text{eff}}$  linearly decreases as

$$U_{\text{eff}}(\Delta) = U_0 - \alpha_\Delta P.$$

The coefficient  $\alpha_\Delta$  can be determined from the condition of crossover of the high-spin ( ${}^6A_1$ ) and low-spin ( ${}^2T_2$ ) terms of the Fe<sup>3+</sup> ion at a critical value ( $P_{\text{cr}}$ ) of the pressure. According to the Tanabe–Sugano diagram (Fig. 3), the critical value of the crystal field parameter is  $\Delta_{\text{cr}} \approx 28.5B = 2.4$  eV, from which it follows that  $\alpha_\Delta =$

$(\Delta_{\text{cr}} - \Delta_0)/P_{\text{cr}} = 0.018$  eV/GPa. The coefficient  $\alpha_t$  can be determined from the experimentally observed increase in  $T_N$  with the pressure [2]. Both the buildup of  $t(P)$  and the decrease in  $U_{\text{eff}}(P)$  lead to the linear increase of the exchange integral  $J(P)$ , so that  $T_N(P)$  can be expressed as

$$T_N(P)/T_N(0) = 1 + (2\alpha_t/t_0 + \alpha_\Delta/U_0)P. \quad (6)$$

According to the experimental data [2],  $T_N(0) = 348$  K and  $T_N(P_{\text{cr}}) \approx 600$  K, this yields  $\alpha_t = 0.00046$  eV/GPa. Taking into account the above estimates of  $U_0 = 4.2$  eV and  $\alpha_\Delta = 0.018$  eV/GPa, we can evaluate the contributions to  $T_N$  due to the band broadening (192 K) and due to the decrease in  $U_{\text{eff}}$  (64 K). Thus, the contribution due to the band broadening is three times that due to the decrease in electron correlations. Nevertheless, the  $d$ -band halfwidth  $W = Zt$  increases rather slightly with pressure: from 0.46 eV at  $P = 0$  to 0.58 eV at  $P = P_{\text{cr}}$ .

As a result of the crossover of the ground-state terms of the  $d^5$  and  $d^4$  electron configurations in the high-pressure phase at  $P = P_{\text{cr}}$ , the energies of the lower and upper Hubbard bands exhibit a change. Denoting these energies by  $\tilde{\Omega}_v$  and  $\tilde{\Omega}_c$ ,

$$\begin{aligned} \tilde{\Omega}_v &= E({}^2T_2, d^5) - E({}^3T_1, d^4), \\ \tilde{\Omega}_c &= E({}^1A_1, d^6) - E({}^2T_2, d^5), \end{aligned} \quad (7)$$

we obtain an expression for the effective Hubbard parameter  $\tilde{U}_{\text{eff}}$ :

$$\tilde{U}_{\text{eff}} = \tilde{\Omega}_c - \tilde{\Omega}_v = A + 9B - 7C. \quad (8)$$

Thus, the parameter  $\tilde{U}_{\text{eff}}$  exhibits a jumplike change at the point of transition, whereby the value at  $P > P_{\text{cr}}$  ( $\tilde{U}_{\text{eff}} = 1.45$  eV) is almost one-third of that at  $P = 0$ . Note that the jump in  $\tilde{U}_{\text{eff}}$  is only due to the crossover of levels and is not related to the structural transition in FeBO<sub>3</sub> [4].

Figure 4 shows the one-electron density of states for both low- and high-pressure phases. As was indicated above, the energies are measured from the top of the valence band of oxygen states (i.e.,  $\epsilon_v = 0$ ). Then, the bottom of the conduction band corresponds to  $\epsilon_c = 2.9$  eV. At a zero applied pressure, we have  $\Omega_v = -1.4$  eV and  $\Omega_c = 2.8$  eV. Figure 5 shows the pressure dependence of the energies  $\epsilon_v$ ,  $\epsilon_c$ ,  $\Omega_v$ , and  $\Omega_c$  in the case of pressure-independent Racah parameters and the crystal field parameter  $\Delta$  linearly increasing with the pressure. Here, we also ignore the possible discontinuity in  $\Delta$  at the point of the structural phase transition. This jump may produce an additional small shift of the  $\tilde{\Omega}_c$  and  $\tilde{\Omega}_v$  bands downward, but  $\tilde{U}_{\text{eff}}$  in the high-pres-

sure phase is independent of  $P$ . The smallness of the jump in  $\Delta$  follows from the experimental fact that the lattice parameter  $c$  changes for the most part gradually in the entire interval  $0 < P < P_{\text{cr}}$  rather than by a jump at  $P_{\text{cr}}$  [4].

According to Fig. 4, single crystal  $\text{FeBO}_3$  in the range of  $P < P_{\text{cr}}$  belongs to the insulators with charge transfer. At  $P > P_{\text{cr}}$ , the insulator character is retained, but the dielectric gap decreases to  $E_{\text{g}} = \tilde{\Omega}_{\text{c}} - W_{\text{d}} - \varepsilon_{\text{v}}$ . For  $P \geq P_{\text{cr}}$ , this leads to  $E_{\text{g}} \approx 0.56$  eV, which allows the material to be considered as a semiconductor. This energy must also determine the edge of optical absorption related to the charge transfer processes. The maximum of absorption is expected at  $\tilde{\Omega}_{\text{c}} - \varepsilon_{\text{v}} \approx 0.85$  eV. A sharp decrease in the absorption edge at pressures above  $P_{\text{cr}}$  is confirmed by the experimental data in Figs. 1 and 2. This drop in the dielectric gap at  $P = P_{\text{cr}}$  indicates that the electronic transition at this pressure is accompanied by the insulator–semiconductor transition.

## 5. EFFECT OF PRESSURE ON THE OPTICAL ABSORPTION SPECTRUM

Since the pressure dependence of parameters  $\Delta(P)$  and  $t(P)$  was determined above from independent (non-optical) data, calculations of the energies of peaks A, B, and C in the optical spectra as functions of the pressure contain no fitting parameters. This provides for the possibility of independent verification of correctness of the proposed model of the electron structure of  $\text{FeBO}_3$  and the effects of pressure predicted by this model.

According to the Tanabe–Sugano diagram, the energies of  ${}^4T_1$  and  ${}^4T_2$  terms decrease almost linearly with increasing crystal field parameter  $\Delta$  and, at the critical point,  $E({}^4T_1, P_{\text{cr}}) = 8\mathbf{B} \approx 0.67$  eV and  $E({}^4T_2, P_{\text{cr}}) = 15.5\mathbf{B} \approx 1.30$  eV. As a result, band A shifts with increasing pressure as  $d\omega_{\text{A}}/dP = -0.0156$  eV/GPa. This can be compared to the experimental pressure-induced decrease in the energy of peak A (Fig. 1b):  $(d\omega_{\text{A}}/dP)_{\text{exp}} = -0.0156$  eV/GPa (see table). For band B, we obtain  $(d\omega_{\text{B}}/dP)_{\text{theor}} = -0.0158$  eV/GPa.

The energy of  ${}^4A_1$  term for  $\text{Fe}^{3+}$ , determining the  $d$ – $d$  exciton energy  $\omega_{\text{C}}$ , is independent of the parameter  $\Delta$ . This agrees well with a weak pressure dependence of the energy of band C observed in experiment (Fig. 1). The energy of excitations with charge transfer,  $\Omega_{\text{C}}$ , slightly decreases with increasing pressure as  $d\Omega_{\text{C}}/dP = -0.4(d\Delta/dP) = -0.0072$  eV/GPa. At  $P = P_{\text{cr}}$  this yields  $\Delta\Omega_{\text{C}} = -0.33$  eV. Probably, it is this small shift that is manifested by a low-energy shoulder observed on band C at high pressures. The most pronounced pressure-induced change in the spectra of a low-pressure phase is the separation of peak C1 from band C. The energy of peak C1 varies most significantly with pressure (Fig. 2). Indeed, according to the Tanabe–Sugano diagram, an increase in pressure in the

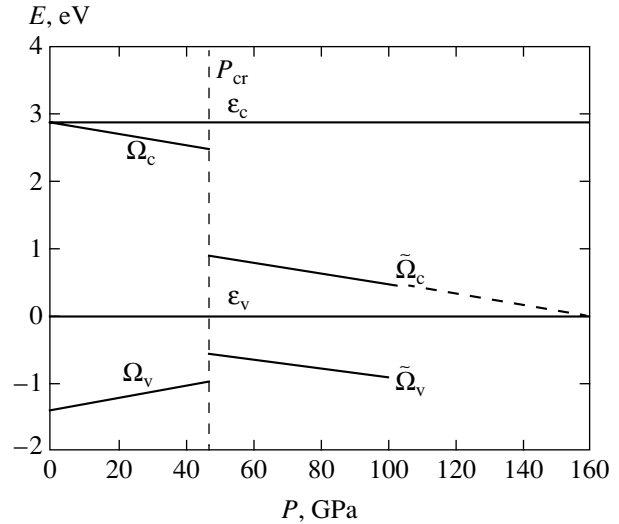


Fig. 5. Shifts of the lower and upper Hubbard bands depending on the pressure in low- and high-pressure phases of single crystal  $\text{FeBO}_3$ .

region of  $P = 0$  is accompanied by the crossover of excited terms  ${}^4A_1$  and  ${}^2A_2$  in  $\text{FeBO}_3$ , which is manifested by a new exciton band at  $\omega_{\text{C1}} = E({}^2A_2) - E({}^4A_1)$ . Since this  $d$ – $d$  transition involves a change in the spin ( $\Delta S = 2$ ), the corresponding intensity is small. At  $P = P_{\text{cr}}$ , experiment (Fig. 2) shows  $\omega_{\text{C1}}(P_{\text{cr}}) = 2.0$  eV and, hence,  $d\omega_{\text{C1}}/dP = -0.0174$  eV/GPa. This is close to the experimental value  $-0.0199$  eV/GPa (see table).

An analogous crossover of terms  ${}^4T_1$  and  ${}^2T_2$  with increasing pressure must lead to an exciton with  $\omega_0 = E({}^2T_2) - E({}^6A_1)$ . This exciton must rapidly shift toward infrared region as  $d\omega_0/dP = -0.030$  eV/GPa, so that  $\omega_0 \approx 0.6$  eV at  $P = 20$  GPa. Being doubly forbidden with respect to spin, a  $\omega_0$  exciton, as well as  $\omega_{\text{C1}}$ , is expected to possess a low intensity. At  $P = P_{\text{cr}}$ , the energy  $\omega_0$  tends to zero. In other words, this exciton plays the role of a “soft” mode for the pressure-induced electronic phase transition.

## 6. PRESSURE-INDUCED TRANSITION: DISCUSSION OF THE MECHANISM

The observed suppression of magnetic properties at high pressures can be explained a priori using various mechanisms. For example, pressure-induced violation of the local symmetry might lead to the rotation of electron orbitals responsible for the indirect exchange, with the resulting decrease in the indirect exchange interaction. However, as was pointed out in Section 2, in our case the pressure is quasi-hydrostatic and the local symmetry of  $\text{Fe}^{3+}$  can be considered unchanged. In addition, the observed increase in the Néel temperature with increasing pressure is indicative of enhanced (rather than reduced) exchange interaction.

An alternative approach to explanation of the magnetic collapse in monoxides (FeO, MnO, CoO, and NiO) was suggested by Cohen *et al.* [17] within the framework of *ab initio* calculations performed in the local density and generalized gradient approximations using the generalized Stoner model. It was concluded that the dominating role is played by the  $d$ -band broadening, which leads to the magnetic collapse and the insulator–metal transition. Indeed, a decrease in the interatomic distances leads to an increase in the  $d$ – $d$  hopping parameter  $t$ , so that the Mott–Hubbard insulator with  $U \gg W = Zt$  at  $P = 0$  may pass to the metallic state with increasing pressure when  $W \geq U$ . It should be noted that this conclusion is based on the Hubbard model in which  $d$  electrons exhibit no orbital degeneracy.

The model proposed in [5] is essentially a generalization of the Hubbard model with allowance of the real orbital structure of  $\text{Fe}^{3+}$ , which leads to the possible coexistence of various spin and orbital multiplets. Since the energies of these multiplets depend on the crystal field parameter  $\Delta$ , a new mechanism appears for the crossover of optical terms as described by the Tanabe–Sugano diagrams. Of course, the  $d$ -band broadening still influences the electron structure. Estimations presented in Section 4 showed that the  $d$  bandwidth in  $\text{FeBO}_3$  rather insignificantly increases with the pressure, and the main mechanism of magnetic collapse is the crossover from high- to low-spin state. As a result, the effective Hubbard parameter  $U_{\text{eff}}$  decreases, as can be seen from Fig. 5 and formulas (3) and (4), with increasing  $\Delta$  and  $P$ . This implies that an increase in the pressure decreases the role of correlations. The  $d$ -band broadening also contributes to a decrease in the dielectric gap, but this effect is small as compared to the influence of decreasing  $U_{\text{eff}}$ .

At pressures above  $P_{\text{cr}}$ , the ground-state terms of  $d^4$ ,  $d^5$ , and  $d^6$  ions are altered, which leads to a jump-like change in the values of  $U_{\text{eff}}$  and the dielectric gap, that is, to the transition of  $\text{FeBO}_3$  crystal to a semiconducting state. As the pressure  $P$  grows further, we may expect a transition to the metallic state to take place. Since the  $U_{\text{eff}}$  value at  $P > P_{\text{cr}}$  no longer depends on the pressure, while the  $d$  bandwidth linearly increases with  $P$ , an insulator–metal transition of the Mott–Hubbard type becomes possible. Once the baric derivative of  $\alpha_t$  is known, we can readily evaluate the critical Mott–Hubbard pressure  $P_{\text{MH}}$  at which the complete metallization takes place and  $W(P_{\text{MH}}) = \tilde{U}_{\text{eff}} = 1.45$  eV, which yields  $P_{\text{MH}} = 360$  GPa. On the other hand, it is interesting to note that extrapolation of the  $\tilde{\Omega}_c(P)$  plot in Fig. 5 to the intersection with the top ( $\varepsilon_v$ ) of the valence band yields  $P_{\text{met}} = 200$  GPa. This value virtually coincides with the experimental estimate of the pressure  $P_{\text{met}} = 210$  GPa for the complete metallization, obtained by extrapolating the thermoactivation gap to zero [3]. However, the transition to the metallic state in this

model should be expected at lower pressures, since the  $E_g$  value tends to zero not only due to a decrease in  $\tilde{\Omega}_c$ , but also due to an increase in the  $d$  bandwidth  $W_d$  (additionally decreasing the gap). In such cases, a transition to the metallic state is caused merely by the crossover of bands due to an increase in the pressure, since the Fermi level must occur below the top of the valence band and the Fermi surface will open. According to Lifshits *et al.* [18], this process is classified as the 2.5-order transition. Taking into account the baric derivatives of  $\alpha_t$  and  $\alpha_\Delta$  determined from the optical and magnetic data for the low-pressure phase, we can estimate the metallization pressure as  $P_{\text{met}} \approx 73$  GPa. However, experiments [3] show that  $\text{FeBO}_3$  at this pressure still occurs in a semiconducting state. Apparently, extrapolation of the baric derivatives of  $\alpha_t$  and  $\alpha_\Delta$  determined for the low-pressure phase to the region of high pressures does not provide for sufficiently accurate evaluation.

## 7. CONCLUSIONS

The band structure and optical spectra of the Mott–Hubbard insulators (including  $\text{FeBO}_3$ ) must depend on the pressure mostly for two reasons: (i) a growth in the pressure may give rise to the  $d$  bandwidth due to an increase in the integral of interatomic electron hopping and (ii) pressure variations alter the crystal field. The results of our calculations taking into account peculiarities of the crystal structure of  $\text{FeBO}_3$  lead to a conclusion that a determining role is played by the pressure-induced change in the crystal field parameter  $\Delta$ . The main peculiarity in the crystal structure of  $\text{FeBO}_3$  is very strong  $s$ – $p$  hybridization inside the  $\text{BO}_3$  group, which leads to a very weak  $p$ – $d$  hybridization between oxygen and iron ions and to a small width of the  $d$  band. The  $d$  band exhibits additional narrowing in the antiferromagnetic phase due to the spin–polaron interaction.

The increase in  $\Delta$  not only leads to the crossover of high- and low-spin states of  $\text{Fe}^{3+}$  ion, explaining the collapse of the magnetic moment, but also causes an analogous crossover of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{4+}$  configurations. As a result, the effective Hubbard parameter

$$U_{\text{eff}} = E_0(d^4) + E_0(d^6) - 2E_0(d^5),$$

which is a measure of the Coulomb correlations, is determined in the low-pressure phase by the high-spin terms of the ground states of  $d^4$ ,  $d^5$ , and  $d^6$  configurations, and in the high-pressure phase, by the corresponding low-spin terms, which accounts for a jump-like decrease in  $U_{\text{eff}}$  at the point of transition. Although  $U_{\text{eff}}$  decreases by a factor of almost three, the metallization does not take place because of a small  $d$  bandwidth. As the pressure grows further, a transition of  $\text{FeBO}_3$  to the metallic state unavoidably takes place. It is interesting to note that extrapolation of the  $\tilde{\Omega}_c$  level to inter-

section with the top of the valence band allows the pressure required for a transition to the metallic state to be estimated as  $P_{\text{met}} = 200$  GPa. This estimate nearly coincides with the experimental value evaluated from the condition of zero thermoactivation gap [3]. However, such extrapolation fully ignores the contribution of the  $d$ -band broadening to a decrease in the dielectric gap. On the other hand, extrapolation of the pressure-induced band broadening determined for the low-pressure phase to the region of high pressures gives an obviously understated value of  $P_{\text{met}} = 73$  GPa. Apparently, the  $d$  bandwidth in the high-pressure phase grows with the pressure slower than in the low-pressure phase. It is also possible that the top of the valence band slightly decreases with increasing pressure, which leads to an increase in  $P_{\text{met}}$ .

Within the framework of our analysis of the pressure dependence of the positions of optical absorption bands (in the low-pressure phase), let us compare the experimental and theoretical data presented in the third and fifth columns of the table, respectively. As can be seen, there is qualitative agreement for all bands in the absorption spectrum of  $\text{FeBO}_3$ . The linear variation of the energies of bands A and B with the pressure confirms the hypothesis of a linear pressure dependence of the crystal field (formula (1)). At the same time, we would like to point out that there is no quantitative agreement between theory and experiment for bands A and B, and the reasons for this discrepancy are unclear. The most unusual feature in the behavior of experimental optical spectra is the separation of peak C1 (most significantly changing with the pressure) from band C. For this peak, found to be related to the  ${}^6A_1 \rightarrow {}^2A_2$  exciton, we observed the best agreement between theory and experiment. On the other hand, it is unclear why the expected exciton  ${}^6A_1 \rightarrow {}^2T_2$  with an energy below that of band A is not observed. This very exciton must play the role of a soft mode for the pressure-induced electronic phase transition, since the transition is due to the crossover of  ${}^6A_1$  and  ${}^2T_2$  terms of  $\text{Fe}^{3+}$  ion.

In conclusion, it should be noted that the proposed many-electron model of the electron structure of  $\text{FeBO}_3$  taking into account strong electron correlations not only qualitatively describes the very fact of the pressure-induced electronic and magnetic transitions, but also explains fine experimental details such as variations in the optical spectra that depend on the pressure.

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