
**MAGNETISM
AND FERROELECTRICITY**

Analysis of the Electrical and Optical Properties of VBO_3 Single Crystals and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ Solid Solutions on the Basis of a Many-Electron Model of Energy Band Structure

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Abstract—A many-electron model of the energy band structure of VBO_3 and of $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions is proposed with strong electron correlations taken into account. Experimental optical absorption spectra and data on the resistivity are discussed in the framework of the suggested model. Variation in the magnetic and electronic properties of VBO_3 and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ under high pressure is predicted. For VBO_3 , a Mott–Hubbard (insulator–metal) transition is expected in the high-pressure phase. In $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions, a nontrivial variation in the properties is predicted, leading to the appearance of a different magnetic state. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

After the discovery of high-temperature superconductivity in copper oxides, interest in the study of strongly correlated electronic systems has increased substantially. Transition-metal borates form yet another class of oxides, whose magnetic and electrical properties are determined by strong electron correlations in narrow d bands. Transition-metal oxyborates $M\text{BO}_3$ (where $M = \text{Fe}, \text{V}, \text{Cr}, \text{Ti}$) crystallize in the calcite structure [space group $R\bar{3}c$ (D_{3d}^6)]. In this class of materials, iron borate, FeBO_3 , has been studied most extensively. This compound was first synthesized in 1963 [1], but correct interpretation of its magnetic properties was given only in 1968, when Joubert and coworkers showed that FeBO_3 belongs to a large class of antiferromagnets with weak ferromagnetism [2]. FeBO_3 is one of the few compounds that have a spontaneous magnetic moment at room temperature and, at the same time, are transparent in the visible part of the spectrum [3, 4]. Such a combination of magnetic and optical properties makes this material rather promising for applications in magneto-optics [5–7]. Although FeBO_3 has been intensively studied for a long time, there are only a few theoretical and experimental investigations into the other representatives of this class, as well as of FeBO_3 -based solid solutions. In particular, there is no information about their electronic and, in some cases, magnetic structure. The optical properties and anisotropy of these compounds have been studied to an even

lesser extent. The VBO_3 , CrBO_3 , and TiBO_3 isostructural compounds were synthesized for the first time in 1964 [8]. Further measurements have shown that CrBO_3 is a low-temperature antiferromagnet ($T_N = 15$ K); according to [9], the magnetic moments of the sublattices are oriented along the third-order C_3 axis. The magnetic and electrical properties of TiBO_3 were recently studied in [10], and it was assumed that this compound is a weak ferromagnet ($T_N = 25$ K). To date, the following systems among the FeBO_3 -based solid solutions have been synthesized and partly investigated: $\text{Fe}_{1-x}\text{Ga}_x\text{BO}_3$ [1, 11–14], $\text{Fe}_{1-x}\text{Al}_x\text{BO}_3$ [13–15], $\text{Fe}_{1-x}\text{Cr}_x\text{BO}_3$ [1, 13, 14, 16, 17], and $\text{Fe}_{1-x}M_x\text{BO}_3$ with $M = \text{Mn}, \text{In}$ [14] and $M = \text{Mg}, \text{Cu}$ [18, 19]

A few studies of FeBO_3 -based solid solutions containing a transition metal as a substitution ion are restricted to the $\text{Fe}_{1-x}M_x\text{BO}_3$ ($M = \text{Mn}, \text{Cr}$) series; however, by synthesizing solid solutions of isostructural compounds having different transport and magnetic properties, one can intentionally create a situation where competing mechanisms and interactions result in the establishment of magnetic order accompanied by a modification of the electrical properties of the sample. Earlier, we performed a complex study of the electrical, magnetic, and optical properties of $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions [20, 21]. The choice of the V^{3+} ion as a substitution ion is motivated by the large difference in the electrical and magnetic properties of the final compounds. For example, FeBO_3 is an antiferromagnet

with weak ferromagnetism ($T_N = 348$ K) and an insulator with an optical absorption edge $E_g = 2.9$ eV [22], while VBO_3 is a ferromagnet ($T_C = 32$ K) and a semiconductor [9].

In spite of the significant advances made in simulation methods, there are no consistent calculations of the energy band structure of transition-metal borates that would even qualitatively account for the interrelation of the observed effects. For this reason, the experimental results were mainly interpreted on the basis of a model. In the case of $3d$ -metal borates, this model was the Mott–Hubbard model. Theoretical studies of the electronic structure of the materials in question are quite scarce and deal mainly with iron borate, FeBO_3 . One-electron *ab initio* calculations of FeBO_3 using the method of the local spin density functional (LDA) and the generalized gradient approximation (GGA) taking into account nonlocal corrections to the L-DA were performed in [23] and [24], respectively. Calculations of the molecular orbitals for the VB_6O_6 and FeB_6O_6 clusters have shown that for both compounds a strong hybridization of s and p cation states with oxygen p states and boron sp states occurs [20]. The valence band is formed by strongly hybridized boron and oxygen s and p states. At the same time, hybridization of the cation d electrons with oxygen s and p electrons is very weak, much weaker than in $3d$ -metal oxides. This is due to strong hybridization in the trigonal BO_3 group. Recently, a collapse of the magnetic moment was observed in iron borate, which was accompanied by a structural transition and modification of the electrical properties of the sample under pressure [25–27]. A many-electron model of the energy band structure of FeBO_3 with allowance for strong electron correlations that adequately describes the transition under pressure was given in [28]. However, up to now, there has been no model of the electronic structure of solid solutions describing the observed properties of these systems and the dynamics of their variation at different concentrations x and pressures.

In this study, we discuss the electrical and optical properties of VBO_3 and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ single crystals on the basis of the many-electron theory of energy band structure taking into account strong electron correlations for these crystals.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

We studied single crystals of VBO_3 and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions grown by spontaneous crystallization from a melt solution [20]. It should be noted that we previously listed the concentrations x determined from the content of the components in the charge (x_s) [20, 21]. To determine the exact amount of the components, we used energy dispersive x-ray analysis (EDAX ZAF Quantification). The values of x obtained and, for com-

Table 1. Vanadium concentrations in $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions (x_s is determined from the charge composition; x , from the data from energy dispersive x-ray analysis)

x_s	x
0.25	0.02
0.5	0.13
0.6	0.18
0.75	0.3
0.95	0.95

parison, the values of x_s used previously are listed in Table 1.

Since the intermediate contact resistance is rather small, resistance measurements were performed by the two-probe method using a teraohmmeter E6-13A, which made it possible to measure resistances of up to 10^{13} Ω . Samples were heated and cooled at a rate of 1 K/min in order to prevent a parasitic temperature gradient.

Single crystals of the $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ series were transparent hexahedral plates with the optical C_3 axis perpendicular to the plate plane. The color of the samples varied from light green (FeBO_3) to dark brown (VBO_3). The optical absorption of the crystals was measured using a single-beam technique in the spectral range 4000–20000 cm^{-1} . The spectral width of the slit of a grating monochromator was 10 cm^{-1} . The accuracy of the absorption measurements was 3%. The spectral resolution varied from 20 cm^{-1} at 20000 cm^{-1} to 13 cm^{-1} at 4000 cm^{-1} .

3. MODEL OF THE VBO_3 BAND STRUCTURE

To calculate the one-electron density of states $N(E)$ in VBO_3 with allowance for strong electronic correlations in the framework of many-electron theory [28], we consider the occupied term V^{3+} ($3d^2$) and the $3d^1$ and $3d^3$ terms describing the annihilation and creation of an electron from the d^2 state. The Hamiltonian of the model is

$$H_{am} = \sum_{\lambda\sigma} \left(\epsilon_{\lambda} n_{\lambda\sigma} + \frac{U_{\lambda}}{2} n_{\lambda\sigma} n_{\lambda\bar{\sigma}} \right) + \sum_{\substack{\lambda, \lambda' \\ (\lambda \neq \lambda')}} \sum_{\sigma\sigma'} (V_{\lambda\lambda'} n_{\lambda\sigma} n_{\lambda'\sigma'} - J_{\lambda\lambda'} a_{\lambda\sigma}^+ a_{\lambda'\sigma'}^+ a_{\lambda'\sigma} a_{\lambda\sigma}), \quad (1)$$

where $n_{\lambda\sigma} = a_{\lambda\sigma}^+ a_{\lambda\sigma}$, $a_{\lambda\sigma}$ is the d electron creation operator in one of the five orbitals λ with spin projection σ , and $\bar{\sigma} = -\sigma$. The first term describes the atomic d levels in the crystalline field; we neglect the small uniaxial

Table 2. Energies $E_S(n)$ of the ground and first excited states of vanadium ions (the subscript denotes spin; n is the electronic configuration)

d^1	d^2	d^3
$E_{1/2}(1) = \epsilon_d - \frac{2}{5}\Delta$	$E_1(2) = 2\epsilon_d - \frac{4}{5}\Delta + V - J$	$E_{3/2}(3) = 3\epsilon_d - \frac{6}{5}\Delta + 3V - 3J$
$E'_{1/2}(1) = \epsilon_d + \frac{3}{5}\Delta$	$E'_1(2) = 2\epsilon_d + \frac{1}{5}\Delta + V - J$	$E'_{3/2}(3) = 3\epsilon_d - \frac{1}{5}\Delta + 3V - 3J$

component of the crystalline field and set $\epsilon(t_{2g}) = \epsilon_d - 2\Delta/5$ and $\epsilon(e_g) = \epsilon_d + 3\Delta/5$. The remaining terms in Eq. (1) correspond to the Coulomb intraorbit repulsion U_λ , interorbit repulsion $V_{\lambda\lambda'}$, and Hund exchange $J_{\lambda\lambda'}$. For simplicity, we disregard the orbital dependence of the Coulomb matrix elements and assume that there are three parameters, U , V , and J , related by the well-known

formula $U = 3V + J$, which follows from the spherical symmetry of the atom.

Since the M - O distances in the VBO_3 and $FeBO_3$ octahedrons are approximately equal, we assume that the Coulomb parameters U , V , and J have the same values as in $FeBO_3$. Furthermore, we assume that the energy of the crystalline field Δ for VBO_3 is close to $\Delta = 1$ eV for $FeBO_3$. Strongly hybridized s and p states of the BO_3 group show almost no change [20]. Thus, we can assume that the bottom of the conduction band ϵ_c and the top of the valence band ϵ_v in VBO_3 are also close in energy, with the energy distance between them (the absorption threshold) being $E_{g0} = 2.9$ eV.

Table 2 lists the energies $E_S(n)$ of the ground and first d^n excited terms with $n = 1, 2, 3$ for vanadium ions with spin S calculated in the strong crystalline field approximation. We find the crystalline field parameter from the optical absorption spectrum of VBO_3 (Fig. 1a), where a low-intensity peak is observed at the energy $\omega_0 = 9800$ cm^{-1} [20]. If we assume, by analogy with $FeBO_3$, that this peak is related to $d-d$ transitions (in this case, transitions occur from the ground-state term 3T_1 of the V^{3+} ion to the first excited term 3T_2 with energy $\omega_0 = E'_1(2) - E_1(2) = \Delta$), then we obtain $\Delta = 1.21$ eV. This value is smaller than the quantity $\Delta = 1.57$ eV for $FeBO_3$ [29]. Furthermore, we assume that the values of the Coulomb parameters U , V , and J are close to the analogous parameters for $FeBO_3$; according to [30], $U = 3$ eV, $V = 1.15$ eV, and $J = 0.7$ eV.

The levels Ω_v and Ω_c are analogous to the lower and upper Hubbard bands for a zero interatomic hopping parameter t :

$$\Omega_v = E_1(2) - E_{1/2}(1) = \epsilon_d - \frac{2}{5}\Delta + V - J, \quad (2)$$

$$\Omega_c = E_{3/2}(3) - E_1(2) = \epsilon_d - \frac{2}{5}\Delta + 2V - 2J.$$

The effective Hubbard energy is defined as the energy of transitions between the lower and upper Hubbard bands:

$$U_{\text{eff}} = \Omega_c - \Omega_v = E_{3/2}(3) + E_{1/2}(1) - 2E_1(2) = V - J. \quad (3)$$

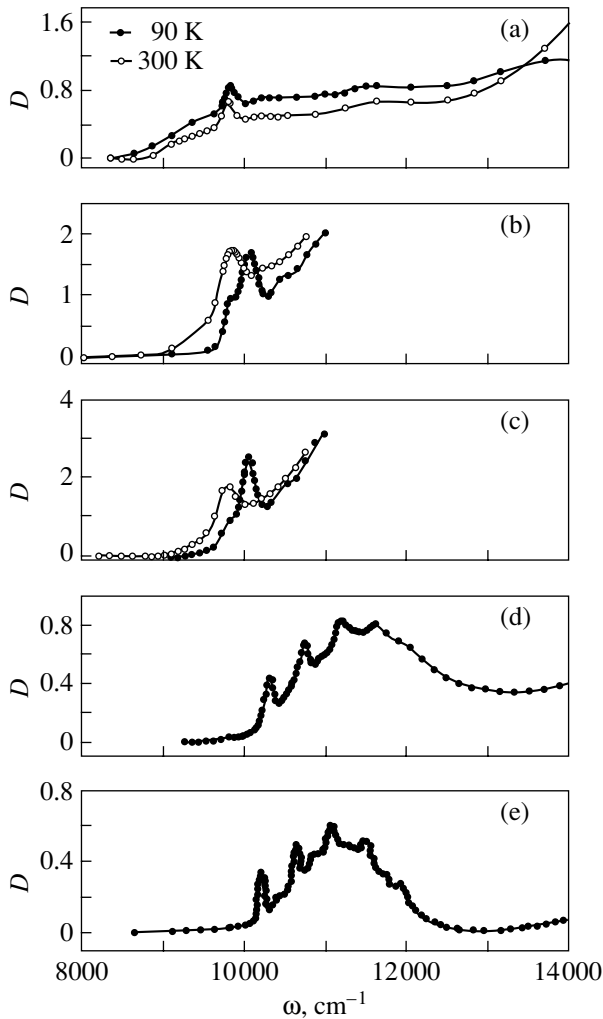


Fig. 1. Optical absorption spectra of solid solutions of the system $Fe_{1-x}V_xBO_3$. (a) VBO_3 , (b) $Fe_{0.7}V_{0.3}BO_3$, (c) $Fe_{0.82}V_{0.18}BO_3$, (d) $Fe_{0.98}V_{0.02}BO_3$, and (e) $FeBO_3$.

Using the parameters U , V , and J defined above, we obtain $U_{\text{eff}} = 0.45$ eV. The lower level Ω_v is occupied, and the upper level Ω_c is empty; this follows from the self-consistency condition on the chemical potential, which can be written in the x representation in the form

$$n_e = \frac{N_e}{N} = 1 \sum_p X^{1p, 1p} + 2 \sum_p X^{2p, 2p} + 3 \sum_p X^{3p, 3p}. \quad (4)$$

Here, $X^{np, n'p'} \equiv |np\rangle\langle n'p'|$ are the Hubbard operators constructed using the many-electron basis of terms $|np\rangle$ (p is the set of spin and orbital indices for an n -electron term).

To correlate the level positions with that of the valence band top of the oxygen p states, we use the data on the conductivity, according to which the activation energy is $E_a = 0.9$ eV. Since the Ω_v and Ω_c states are localized and do not contribute to the conductivity, the quantity $2E_a$ can be correlated with the energy of charge transfer excitations with $\Omega_c - \varepsilon_v (p^6 d^2 \rightarrow p^5 d^3)$ (in this case, a hole appears on an oxygen atom at the top of the valence band and an electron appears at the level Ω_c ; i.e., a V^{2+} ion is formed). Measuring the one-particle energy from the valence band top, we obtain $\Omega_c = 1.8$ eV and $\Omega_v = 1.35$ eV. The density of states $N(E)$ for VBO_3 is represented schematically in Fig. 2. According to the classification used by Zaanen *et al.* [31], VBO_3 can be considered a Mott–Hubbard insulator.

In addition to the levels Ω_v and Ω_c with a spectral weight of 1, virtual levels with zero spectral weight in the stoichiometric ground state appear in the many-electron approach [32]. Such states acquire a nonzero spectral weight at deviations from stoichiometry or under optical pumping of excited levels. In the case of VBO_3 , inside the band gap, we have the virtual level

$$\Omega'_v = E'_1(2) - E_{1/2}(1) = \Omega_v + \Delta = 2.56 \text{ eV},$$

shown by the dashed line in Fig. 2. Such levels do not contribute to $N(E)$, but optical transitions involving these levels are possible; therefore, they can be expected to appear in the absorption spectrum.

4. BAND STRUCTURE OF $Fe_{1-x}V_xBO_3$ SOLID SOLUTIONS

When simulating the electronic structure of $Fe_{1-x}V_xBO_3$ solid solutions, we make the following assumptions. First, the BO_3 states and, therefore, the parameters ε_c , ε_v , and $E_{g0} = \varepsilon_c - \varepsilon_v$ are assumed to be constant for all x . Second, the distribution of d electrons in the crystal can be spatially homogeneous or inhomogeneous; in any case, the average concentration of d electrons is $n_d = 5 - 3x$. We consider both possibilities.

In the case of a homogeneous distribution, the electron concentration per cation is $\langle n_d \rangle = n_d$. Such a distri-

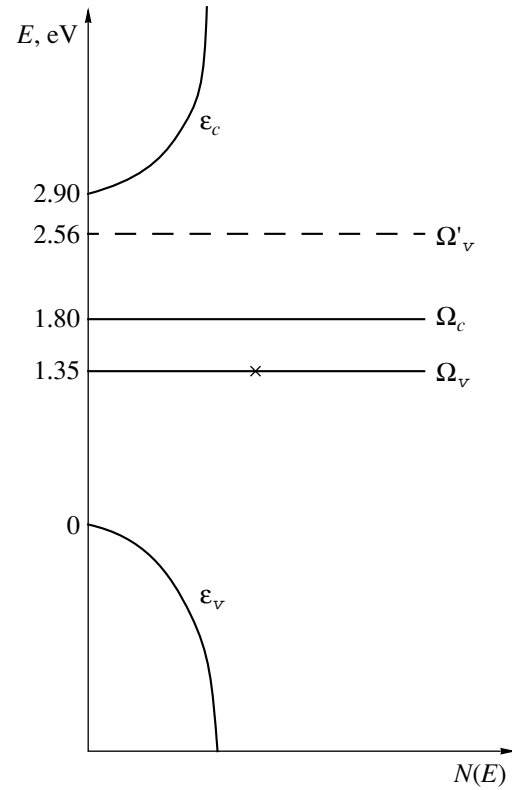


Fig. 2. Density of states for VBO_3 (schematic).

bution could be established in a metal alloy due to hopping of d electrons between the cations. However, in our case, where the hopping integral t_d is almost zero, there is no reason to expect the electron distribution to be homogeneous. Nevertheless, we consider a possible optical spectrum for the “homogeneous scenario.” As follows from the self-consistency condition for the chemical potential, the occupation probability for the d^5 configuration with spin $5/2$ is $N_{5/2}(d^5) = 1 - 3x$ for $x < 1/3$. The lower term d^4 with spin $S = 2$ is occupied with the probability $N_2(d^4) = 3x$. Thus, the optical absorption spectrum can be written in the form

$$I(\omega) = N_{5/2}(d^5)\delta(\omega - \varepsilon_A) + N_2(d^4)\delta(\omega - \tilde{\varepsilon}), \quad (5)$$

where $\varepsilon_A = E_{3/2}(5) - E_{5/2}(5)$ is the energy of an exciton ${}^6A_{1g}(S = 5/2) \rightarrow {}^4T_{1g}(S = 3/2)$, which determines the A absorption band in $FeBO_3$, and $\tilde{\varepsilon} = E({}^3T_1) - E({}^5E)$ is the exciton energy for the d^4 configuration. Using Tanabe–Sugano diagrams and the above value of the parameter Δ , we find $\tilde{\varepsilon} = 0.97$ eV. We did not detect an exciton with this energy in the $Fe_{1-x}V_xBO_3$ optical spectra. Thus, the assumption of a homogeneous distribution does not agree with the experimental data.

In the model of an inhomogeneous distribution, we assumed a random spatial distribution of the two types of cations: V^{3+} (d^2) with probability x and Fe^{3+} (d^5) with

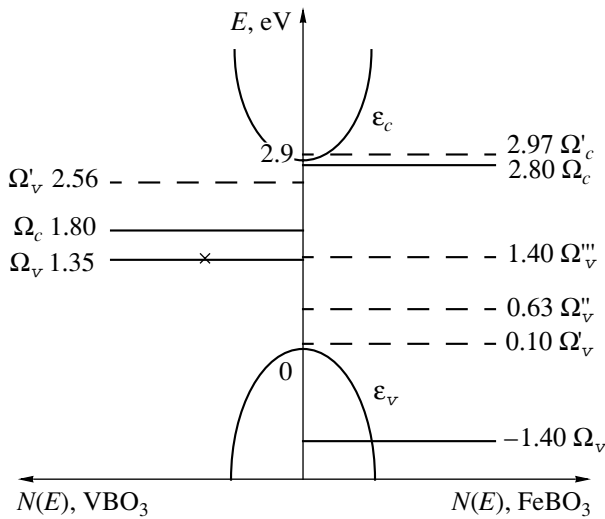


Fig. 3. Density of states for $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions (schematic). The left part is to be taken with weight x , and the right part, with weight $(1-x)$.

probability $1-x$. In this model, characteristics such as the density of states, the optical spectrum, and the Mössbauer effect can be written in the form

$$\begin{aligned} N(E) &= xN_V(E) + (1-x)N_{\text{Fe}}(E), \\ D(\omega) &= xD_V(E) + (1-x)D_{\text{Fe}}(E), \end{aligned} \quad (6)$$

where $N_V(N_{\text{Fe}})$ and $D_V(D_{\text{Fe}})$ are the density of states and the absorption intensity for VBO_3 (FeBO_3). The density

of states for $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions is shown schematically in Fig. 3; the density of states for FeBO_3 is taken from [30].

Let us consider the concentration dependence of the optical absorption spectra for solid solutions of the $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ series. For $x = 0.02$, the contribution from I_V is negligible and the spectrum in Fig. 1d practically coincides with the spectrum for FeBO_3 . For comparison, Figs. 4 and 5 show the experimental absorption spectra for the solid solutions and the simulated spectra calculated by using Eq. (6) under the assumption of independent V^{3+} and Fe^{3+} absorption centers. For $x = 0.18$, we can distinguish the same spectral lines A_1 – A_4 as for FeBO_3 , but these lines are strongly broadened (Fig. 4a). The absorption line $\epsilon_A = 9800 \text{ cm}^{-1}$ for VBO_3 is seen as a wide shoulder on the slope of the peak A_1 ; the latter is shifted by 100 cm^{-1} to lower energies as compared to FeBO_3 . We believe that the reason for this shift is a change in the magnetic order. Indeed, due to the interatomic exchange interaction I , the energy of the $E_S(n)$ term depends on the spin projection M :

$$E_{S,M}(n) = E_S - I\langle S^Z \rangle M. \quad (7)$$

Estimation of the exchange integral yields a value of $I \approx 120 \text{ cm}^{-1}$ [30]. Accordingly, the maximum shift of the exciton energy is $\epsilon_A \approx I\langle S^Z \rangle \approx \frac{5}{2}I = 300 \text{ cm}^{-1}$. In the original FeBO_3 at low temperatures, we have $\epsilon_A = 10250 \text{ cm}^{-1}$, whereas at $T > T_N = 348 \text{ K}$ we have $\epsilon_A =$

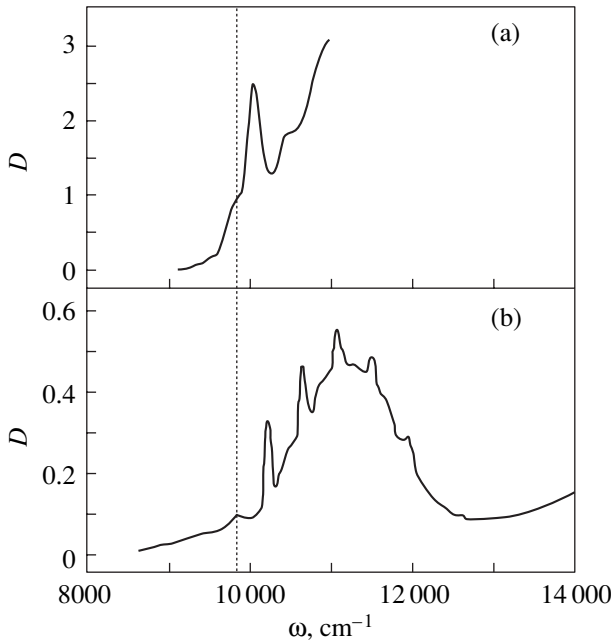


Fig. 4. Optical absorption spectra of $\text{Fe}_{0.82}\text{V}_{0.18}\text{BO}_3$ at $T = 90 \text{ K}$. (a) Experimental data, and (b) the calculated spectrum.

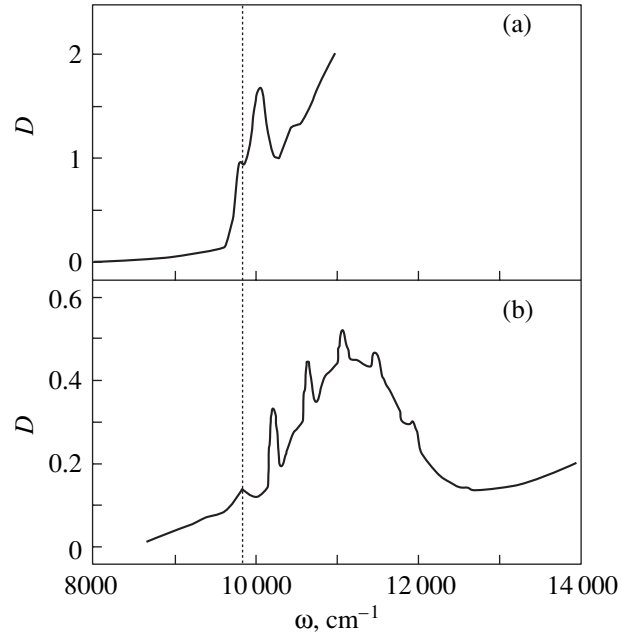


Fig. 5. Optical absorption spectra of $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$ at $T = 90 \text{ K}$. (a) Experimental data, and (b) the calculated spectrum.

9950 cm^{-1} . For the $\text{Fe}_{0.82}\text{V}_{0.18}\text{BO}_3$ composition, the magnetic order is partially suppressed and T_N drops to 200 K; therefore, the shift $\delta\epsilon_A$ equal to 1/3 of the maximum value agrees with the partial suppression of the magnetic order.

For the $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$ composition, the magnetic order is suppressed even more strongly and there is no magnetic order above 180 K. We note that, in a magnetically ordered state of FeBO_3 , the line $\epsilon_A = 9950 \text{ cm}^{-1}$ is very close to the absorption line $\epsilon_A = 9800 \text{ cm}^{-1}$ for VBO_3 ; therefore, for $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$, the two lines close in energy are superimposed and a broad peak is seen in the absorption spectrum (Fig. 1b). With a decrease in temperature to 90 K, the line ϵ_A is shifted to the energy region near 10050 cm^{-1} due to magnetic ordering and the lines in the absorption spectrum of the $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$ solid solution are split (Fig. 5a). The peak lying lower in energy corresponds to the absorption line of the V^{3+} ion, and the upper peak corresponds to that of the Fe^{3+} ion.

5. VARIATION IN THE BAND STRUCTURE OF VBO_3 AND $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ SOLID SOLUTIONS UNDER PRESSURE

Recent experiments [25–27] have revealed nontrivial variations in the magnetic and electronic properties of FeBO_3 at high pressures, which consist in a collapse of the magnetic moment and a tendency toward metalization. These variations were interpreted in [28] as a result of the crossover of the high-spin term d^5 ($S = 5/2$) and the low-spin term d^5 ($S = 1/2$) with an increase in the crystalline field parameter Δ under pressure. Therefore, possible variations in the properties of VBO_3 and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions with increasing pressure, i.e., with increasing parameter Δ , are of interest.

For VBO_3 , there is no crossover between the ground-state high-spin and low-spin excited terms in any of the sectors of the Hilbert space (d^1 , d^2 , d^3). The magnitude of the Mott–Hubbard band gap $U_{\text{eff}} = \Omega_c - \Omega_v$ does not depend on the parameter Δ . In this case a change in the energy band structure under pressure can only occur through broadening of the d bands and the Mott–Hubbard (insulator–metal) transition.

For $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ solid solutions, an unusual situation is possible where there is a crossover of the Fe^{3+} terms and there is no crossover of the V^{3+} terms. This situation implies that there exists a mixture of $S = 5/2$ (Fe) and $S = 1$ (V) spins below the critical pressure $P_c \approx 50 \text{ GPa}$ and a mixture of $S = 1/2$ (Fe) and $S = 1$ (V) spins above P_c . Since VBO_3 is a ferromagnet and FeBO_3 is expected to be antiferromagnetically ordered above P_c , we may expect that, in the $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ system, ferromagnetic and antiferromagnetic bonds are randomly distributed and are of the same order of magnitude. Such a situation can give rise to disordered magnetic phases, in particular, to a spin glass.

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REFERENCES

1. I. Bernal, C. W. Struck, and J. G. White, *Acta Crystallogr.* **16**, 849 (1963).
2. J. C. Joubert, T. Shirk, W. B. White, and R. Roy, *Mater. Res. Bull.* **3**, 671 (1968).
3. A. J. Kurtzig, R. Wolfe, R. C. LeCraw, and J. W. Nielsen, *J. Appl. Phys.* **14**, 350 (1969).
4. R. Wolfe, A. J. Kurtzig, and R. C. LeCraw, *J. Appl. Phys.* **41**, 1218 (1970).
5. B. Andlauer, J. Schneider, and W. Wettling, *Appl. Phys.* **10**, 189 (1976).
6. V. N. Zabluda, A. V. Malakhovskii, and I. S. Édel'man, *Fiz. Tverd. Tela (Leningrad)* **27**, 133 (1985) [*Sov. Phys. Solid State* **27**, 77 (1985)].
7. J. Haisma, H. J. Prins, and K. L. L. van Mierlo, *J. Phys. D: Appl. Phys.* **7**, 162 (1974).
8. H. Schmid, *Acta Crystallogr.* **17**, 1080 (1964).
9. T. A. Bither, C. G. Frederick, T. E. Gier, J. F. Weiher, and H. S. Young, *Solid State Commun.* **8**, 109 (1970).
10. Xu Ziguang, Matam Mahesh Kumar, and Ye Zuo Guang, in *Proceedings of Annual March Meeting* (Am. Phys. Soc., New York, 2001).
11. N. M. Salanskii, E. A. Glozman, and V. N. Seleznev, *Phys. Status Solidi A* **36**, 779 (1976).
12. I. W. Shepherd, *Phys. Rev. B* **5**, 4524 (1972).
13. M. Vithal and R. Jagannathan, *J. Solid State Chem.* **63**, 16 (1986).
14. O. Muller, M. P. O'Horo, and J. F. O'Neill, *J. Solid State Chem.* **23**, 115 (1978).
15. T. A. Bither and H. S. Young, *J. Solid State Chem.* **6**, 502 (1973).
16. M. P. O'Horo and O. Muller, *J. Appl. Phys.* **49**, 1516 (1978).
17. M. W. Ruckman, R. A. Levy, and R. Chennette, *J. Appl. Phys.* **53**, 1694 (1982).
18. A. A. Karaev, B. Yu. Sokolov, and Yu. M. Fedorov, *Fiz. Tverd. Tela (St. Petersburg)* **42**, 2036 (2000) [*Phys. Solid State* **42**, 2097 (2000)].
19. De Lacklison, J. Chadwick, and J. L. Page, *J. Phys. D: Appl. Phys.* **5**, 810 (1972).
20. N. B. Ivanova, V. V. Rudenko, A. D. Balaev, N. V. Kazak, V. V. Markov, S. G. Ovchinnikov, I. S. Édel'man, A. S. Fedorov, and P. V. Avramov, *Zh. Éksp. Teor. Fiz.* **121**, 354 (2002) [*JETP* **94**, 299 (2002)].
21. V. V. Markov, V. V. Rudenko, I. S. Édel'man, N. B. Ivanova, N. V. Kazak, A. D. Balaev, and S. G. Ovchinnikov, *Phys. Met. Metallogr.* **93**, 114 (2002).

22. I. S. Édel'man, A. V. Malakhovskii, T. I. Vasil'eva, and V. N. Seleznev, *Fiz. Tverd. Tela (Leningrad)* **14**, 2810 (1972) [*Sov. Phys. Solid State* **14**, 2442 (1972)].
23. A. V. Postnikov, St. Bartkowski, M. Neumann, R. A. Rupp, E. Z. Kurmaev, S. N. Shamin, and V. V. Fedorenko, *Phys. Rev. B* **50**, 14849 (1994).
24. K. Parlinski, *Eur. Phys. J. B* **27**, 283 (2002).
25. I. N. Troyan, A. G. Gavrilyuk, V. A. Sarkisyan, I. S. Lyubutin, R. Ruffer, O. Leupold, A. Barla, B. Doyle, and A. I. Chumakov, *Pis'ma Zh. Éksp. Teor. Fiz.* **74**, 26 (2001) [*JETP Lett.* **74**, 24 (2001)].
26. A. G. Gavrilyuk, I. A. Trojan, R. Boehler, M. Eremets, A. Zerr, I. S. Lyubutin, and V. A. Sarkisyan, *Pis'ma Zh. Éksp. Teor. Fiz.* **75**, 25 (2002) [*JETP Lett.* **75**, 23 (2002)].
27. V. A. Sarkisyan, I. A. Trojan, I. S. Lyubutin, A. G. Gavrilyuk, and A. F. Kashuba, *Pis'ma Zh. Éksp. Teor. Fiz.* **76**, 788 (2002) [*JETP Lett.* **76**, 664 (2002)].
28. S. G. Ovchinnikov, *Pis'ma Zh. Éksp. Teor. Fiz.* **77**, 808 (2003) [*JETP Lett.* **77**, 676 (2003)].
29. A. V. Malakhovskii and I. S. Edelman, *Phys. Status Solidi B* **74**, K145 (1976).
30. S. G. Ovchinnikov and V. N. Zabluda, *Zh. Éksp. Teor. Fiz.* (in press).
31. J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
32. V. V. Val'kov and S. G. Ovchinnikov, *Quasiparticles in Strongly Correlated Systems* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2001) [in Russian].

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