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Electronic Transitions in the VBO_3 Single Crystal at High Pressures

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Optical absorption spectra of single crystals of the ferromagnetic semiconductor VBO_3 are studied at high pressures up to 70 GPa achieved in a diamond-anvil cell. An electronic transition accompanied by sharp changes in the optical parameters and a decrease in the optical gap from $E_0 = 3.02$ eV to 2.25 eV is found at the pressure $P_C \approx 30$ GPa. The gap does not disappear in the high-pressure phase and its value becomes typical of semiconductors. This is indicative of a semiconductor–semiconductor transition. The transition to the metallic state may occur at the critical pressure $P_{met} \sim 290$ GPa.

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1. INTRODUCTION

Transition-metal borates $M^{3+}BO_3$ (M^{3+} = Ti, V, Cr, and Fe) have a rhombohedral calcite-like structure with space group $R\bar{3}c(D_{3d}^6)$ [1]. The metal ions in the crystal lattice are located inside oxygen octahedrons on the rhombohedron body diagonals. The boron ions are strongly bonded with three neighboring oxygen ions and form planar triangular anions $(BO_3)^{3-}$. The insulator and magnetic properties of these materials are determined by strong electronic correlations in narrow *d* bands.

Iron borate $FeBO_3$ is the best studied material of this type. A complex study of this crystal at high pressures [2–8] revealed the magnetic-moment collapse at $P \sim 46$ GPa [5, 6] accompanied by an electronic insulator–semiconductor transition with a sharp jump of the optical absorption edge from ~3 eV down to ~0.8 eV [7], and a structural transition at ~53 GPa with a 9% jump of the cell volume [8]. Mössbauer spectra [6] show that the magnetic-moment collapse in $FeBO_3$ is caused by the transition of Fe^{3+} ions from the high- (HS) to low-spin (LS) state. According to the many-electron theory developed in [9, 10], this effect is explained by the crossover of the HS and LS terms caused by an increasing crystal field with an increase in the pressure.

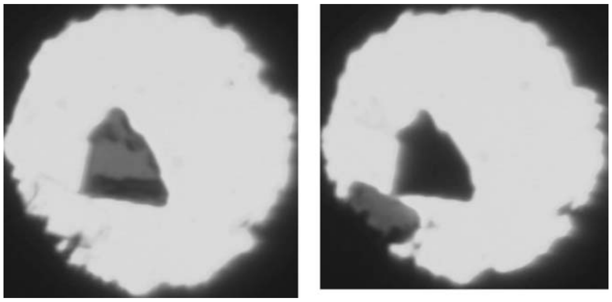
In contrast to the antiferromagnetic insulator $FeBO_3$, vanadium borate VBO_3 under normal pressure is a ferromagnetic semiconductor [11] with the Curie temperature $T_C = 34$ K and the relatively high activation energy $E_a \approx 0.9$ eV [12]. The substitution of Fe^{3+} ions by V^{3+} ions with a similar ion radius makes it possible to obtain isostructural compounds with similar crystal-lattice parameters [13].

This work is devoted to studying the optical absorption spectra of VBO_3 single crystals at high pressures up to 70 GPa achieved in diamond-anvil cells.

2. EXPERIMENTAL SAMPLES AND TECHNIQUE

VBO_3 single crystals were obtained by solution–melt crystallization. The method is described in detail in [14]. These single crystals have the form of thin hexagonal plates with smooth glossy surfaces. The optical axis C_3 was perpendicular to the plate plane. The crystals were transparent and brown in color. The x-ray diffraction measurements confirmed the rhombohedral symmetry group $R\bar{3}c(D_{3d}^6)$ with the lattice parameters $a_H = 4.621$ Å and $c_H = 3.14$ Å, and the cell volume $V = 268.4$ Å^3.

Two plates with different thicknesses were used for the optical measurements in the high-pressure cell. The "thin" sample had the thickness $d \sim 1$–2 μm and plate sizes 20 × 40 μm. The "thick" crystal had the thickness



P = 7.8 GPa P = 69.5 GPa

Fig. 1. Microphotograph of VBO_3 crystals in the working volume of the high-pressure cell. The light spot diameter is about 100 µm. The thick and thin samples are dark-brown and light-yellow at low pressures and become opaque and dark-cherry at high pressures, respectively. One of the ruby crystals is seen near the thick sample.

~10–15 µm and plate sizes 40 × 40 µm. The optical spectra of both crystals at high pressures were measured simultaneously inside the working volume of a diamond-anvil cell.

The anvil diameter was 350 µm. The samples were placed in a 100-µm-diameter hole of a rhenium gasket. The polyethylsiloxane liquid PES-5 ensuring the quasi-hydrostatic compression was used as the pressure medium. The pressure was measured by the standard technique based on the ruby fluorescence line shift. A few ruby crystals with sizes of about 10 µm were placed in the cell working volume near the studied samples. The microphotograph of the experimental assembly is shown in Fig. 1.

The optical absorption spectra were measured in the visible and near-infrared regions (0.4–1.9 µm) at room temperature. An FEU-100 photomultiplier was used as the optical detector. The near-infrared radiation was detected by a liquid nitrogen cooled germanium diode. The halogen lamp light directed perpendicularly to the plate planes was focused on the samples. The light spot diameter on the sample was ~20 µm. The reference signal I_0 outside the sample was first measured. Then, the signal I transmitted through the sample was measured. The optical absorption was calculated according to Bouguer's law $I = I_0\exp(-\alpha d)$, where α is the optical absorption coefficient and d is the sample thickness.

3. OPTICAL SPECTRA AT HIGH PRESSURE

The optical absorption spectra of thin and thick VBO_3 samples observed at various pressures are shown in Figs. 2a and 2b, respectively. A sharp optical-absorp-

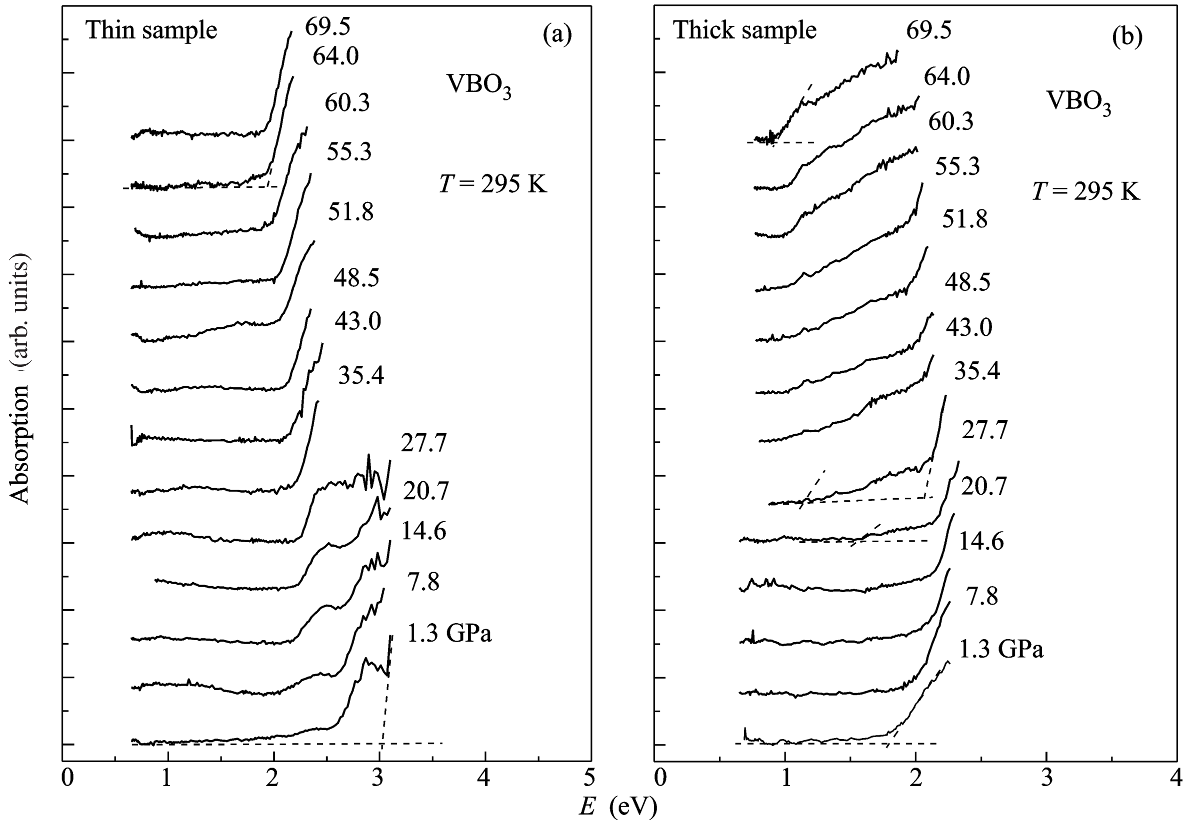


Fig. 2. Optical absorption spectra of the (a) thin and (b) thick VBO_3 samples measured for various pressures and room temperature.

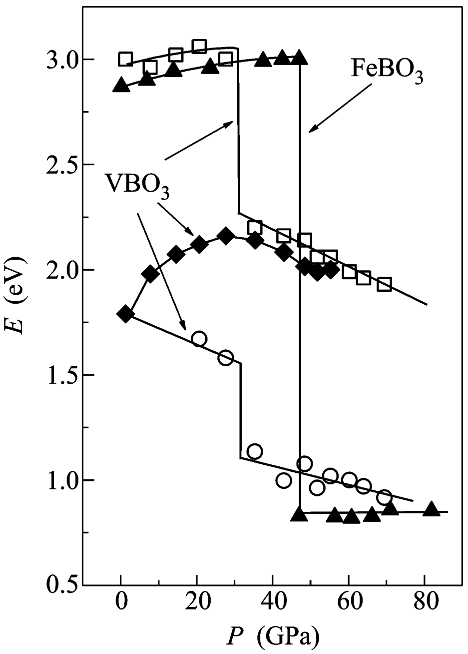


Fig. 3. Pressure dependence of the (squares) strong absorption edge in the thin VBO$_3$ crystal and the (circles) weak and (rhombs) fictitious absorption edges in the thick VBO$_3$ crystal. The behavior of the absorption edge in the FeBO$_3$ single crystal [7] is shown by the triangles.

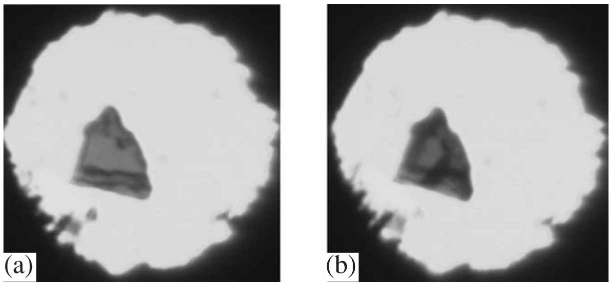


Fig. 4. Changes in VBO$_3$ single crystals at the pressure P = (a) 27.7 and (b) 35.1 GPa. Optical defects are seen, which arise due to the electronic transition at pressures P ~ 30 GPa and are probably associated with a structural phase transition.

tion edge at an energy of ~3.02 eV, which is called the "strong" absorption edge, is observed in the thin sample at the pressure P = 1.3 GPa close to the value 2.9 eV for FeBO$_3$ [7, 15]. Two broad bands with different intensities were observed below the absorption edge energy at ~2.45 and ~2.87 eV. The maximum intensity of the 2.45-eV band increases rapidly with pressure (in particular, by a factor of about 4 with a pressure increase from 1.3 to 27.7 GPa), while the intensity of the 2.87-eV band is almost independent of the pressure. The "tail" of the lower-energy band is transformed into a new absorption edge at 2.25 eV for a pressure of ~30 GPa. This effect looks like an optical gap jump from ~3.02 to 2.25 eV (see Figs. 2a and 3). A further increase in the pressure results in a monotonic downshift of the optical-gap energy to 1.92 eV for P = 69.5 GPa.

The thick sample has a complicated optical absorption spectrum (Fig. 2b). The crystal is opaque above 2.4 eV. The left "shoulder" of the 2.45-eV band clearly observed for the thin sample is seen for E < 2.4 eV. This shoulder in the thick sample forms an "fictitious" absorption edge with an energy of ~1.8 eV. The energy of this edge increases with pressure and becomes close to the strong absorption edge energy for 30 GPa (see Fig. 3). However, this energy for higher pressures from ~30 to ~55 GPa decreases with the same rate as the strong absorption edge in the thin sample. A new absorption band with the maximum at ~1.72 eV is observed for the thick sample with an increase in the pressure. The intensity of this band increases and a new absorption edge with an energy of about 1.5 eV is formed when P is in the interval from 14 to 20 GPa. This absorption edge is called "weak." Note that the new absorption edge has a square root profile. This may be attributed to direct interband transitions. The energy of the weak absorption edge decreases stepwise from ~1.5 to 1.1 eV at the critical pressure P ~ 30 GPa. The intensity of this band increases with a further increase in the pressure and the optical gap gradually downshifts to ~0.94 eV for the maximum pressure ~69.5 GPa.

Figure 3 shows the pressure dependences of the strong absorption edge in the thin sample and the weak and fictitious absorption edges in the thick sample. For comparison, the behavior of the absorption edge in the FeBO$_3$ crystal [7] is shown in this figure. Hence, two fundamental absorption edges can be pointed out: the strong absorption edge for the thin sample and the weak absorption edge for the thick sample. The optical gap decreases in both samples at the critical pressure P_C ~ 30 GPa and the corresponding absorption edge becomes sharp. The absorption-edge jumps are indicative of an electronic transition, which can be attributed to a structural phase transition accompanied by a jump in the crystal-cell volume and, correspondingly, in the crystal-field parameter Δ.

The microphotographs of the thick crystal taken at various pressures with an optical microscope (Fig. 4) provide evidence for possible structural transformations in VBO$_3$ at 30 GPa. The crystal remained homogeneous for P < 30 GPa. However, cracks were observed at pressures immediately above 30 GPa. This can be associated with the structural transformation. The microphotographs in Fig. 4 show the appearance of defects in the thick crystal for P > 30 GPa. X-ray diffraction experiments at high pressures are required to insight into the nature of these transformations.

The electronic transition at P > 30 GPa is followed by linear decreases in the strong and weak absorption edges with an increase in the pressure up to the maximum pressure $P = 69.5$ GPa achieved in our experiment. The linear approximation of the pressure dependence of the optical gap,

$$E(P) = E(0)(1 - P/P_{\text{met}}), \qquad (1)$$

makes it possible to estimate the pressure P_{met} at which the gap vanishes and the complete metallization takes place (see Fig. 5). The linear fit yields the following parameters in the absence of additional transitions:

$E(0) = 2.52 \pm 0.04$ eV and $P_{\text{met}} = 293 \pm 20$ GPa

for the strong absorption edge and

$E(0) = 1.27 \pm 0.08$ eV and $P_{\text{met}} = 260 \pm 50$ GPa

for the weak absorption edge.

Note that the samples changed their colors at the critical pressure. This is clearly seen for the thick sample whose color changed from light- to dark-brown (see Figs. 1 and 4).

4. DISCUSSION OF THE RESULTS

Ab initio calculations of the electronic structure of transition element borates revealed the strong *sp*-hybridization in the BO_3 group. This leads to the weak crossover of the metal and oxygen orbitals, $d(M)$ and p(O). Thus, the integral t of interatomic *d–d* transitions decreases in comparison with typical oxides [14, 16, 17]. Thereby, the carrier-localization condition $U > W$, where U is the Coulomb interaction energy, $W = 2zt$ is the d-band width, and $z = 6$ is the number of nearest neighbors, can be easily satisfied for these materials. Taking into account the “Coulomb” nature of the insulator gap, one can expect that the Mott regime $U < W$ is reached in such systems at high pressures and the insulator–metal transition occurs and results in sharp changes in the magnetic and optical parameters.

The optical measurements carried out in this work for two VBO_3 single crystals of different thicknesses make it possible to observe the features of the optical absorption spectra and the electronic-structure transformations at high pressures. The measured optical gap for the thin sample is $E_0 \approx 3.02$ eV. This is close to the gap width in the $FeBO_3$ crystal.

We propose the following interpretation of the VBO_3 optical spectra obtained in this work. According to the Tanabe–Sugano diagram [18, 19] that shows the splitting of the levels of the V^{3+} ions in the crystal field of cubic symmetry, the vanadium absorption spectrum contains three broad bands corresponding to the intense (allowed) transitions of the V^{3+} ion from the ground term ${}^3T_1$ ($t_{2g}^2e_g^0$) to the excited terms ${}^3T_2$ ($t_{2g}^1e_g^1$), ${}^3T_1$ ($t_{2g}^1e_g^1$), and ${}^3A_2$ ($t_{2g}^0e_g^2$). The crystal field $\Delta = 1.21$ eV for VBO_3 was determined earlier in [11] from the energy peak in the optical absorption spectrum under the assumption that this peak is due to *d–d* transitions from the ground term ${}^3T_1$ to the first excited term ${}^3T_2$. Using the experimental data of this work, three groups of intermediate bands can be pointed out within the gap between the valence and conductance bands. The energies of these bands (2.87, 2.45, and 1.72 eV) correspond to the allowed and forbidden *d–d* transitions from the ground level ${}^3T_1$ of the V^{3+} ion to excited levels.

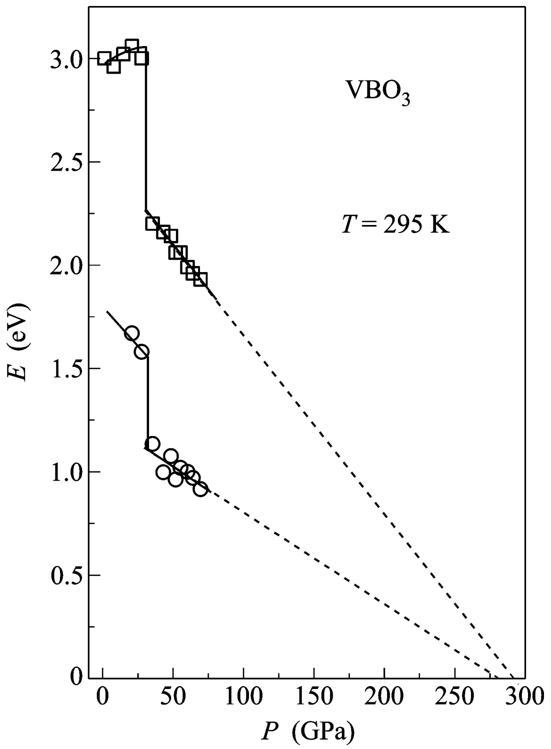


Fig. 5. Linear extrapolation of the pressure dependence of the optical-absorption edges in the thin and thick VBO_3 crystals. The strong and weak absorption edges are shown by the squares and circles, respectively.

The maximum intensity of the band at ~2.87 eV for the low pressure 1.3 GPa is almost an order of magnitude higher than the maximum peak intensity of the band at 2.45 eV. Hence, it is expedient to associate the absorption band at 2.87 eV with the intense allowed *p–d* charge transfer transition from the ground term $t_{2g}^2e_g^0p^6$ (${}^3T_1$) to the level $t_{2g}^2e_g^1p^5$. The intensity of the band at 2.45 eV is strongly dependent on pressure. This band is presumably attributed to the allowed *d–d* transition from the ground term ${}^3T_1$ to the ${}^3A_2$ level with the energy 2Δ. The absorption spectrum of the thick sample exhibits the third broad band at 1.72 eV. The intensity of this band is pressure-dependent. According to the Tanabe–Sugano diagram, the crossover of the ground and excited terms is absent in this energy range. The crystal lattice symmetry can be reduced at a high pressure. Correspondingly, additional splitting of the doubly-degenerate term ${}^1T_2$ can arise. In addition, the large pressure derivative of this band can be indicative of the strong effect of the charge transfer transitions $p^6d^2 \longrightarrow p^5d^3$ from the valence band top on the formation of this band.

We assume that the stepwise changes in all the spectra of the VBO$_3$ crystal at the pressure P_C ~ 30 GPa is probably attributed to a first-order structural phase transition resulting in a stepwise increase in the parameters Δ and t dependent on the interatomic distance.

In conclusion, we note that the data on the optical absorption in the VBO$_3$ crystal imply that an electronic transition accompanied by sharp changes in the optical parameters and a decrease in the optical gap from E_0 = 3.02 eV to 2.25 eV occurs at P_C ~ 30 GPa. The fact that E_0 does not vanish in the high-pressure phase but has the value typical of semiconductors is indicative of a semiconductor–semiconductor transition. The transition to the metallic state is possible at the critical pressure P_{met} ~ 290 GPa.

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REFERENCES

1. I. Bernal, C. W. Struck, and J. G. White, Acta Cryst. **16**, 849 (1963).
2. I. S. Lyubutin, V. A. Sarkisyan, A. G. Gavriliuk, et al., Izv. Ross. Akad. Nauk, Ser. Fiz. **67**, 1018 (2003).
3. A. G. Gavriliuk, I. A. Trojan, S. G. Ovchinnikov, and I. S. Lyubutin, Zh. Eksp. Teor. Fiz. **126**, 650 (2004) [JETP **99**, 566 (2004)].
4. A. G. Gavriliuk, I. A. Trojan, I. S. Lyubutin, et al., Zh. Eksp. Teor. Fiz. **127**, 780 (2005) [JETP **100**, 688 (2005)].
5. I. A. Trojan, A. G. Gavriliuk, I. S. Lyubutin, et al., Pis’ma Zh. Eksp. Teor. Fiz. **74**, 26 (2001) [JETP Lett. **74**, 24 (2001)].
6. V. A. Sarkisyan, I. A. Trojan, I. S. Lyubutin, et al., Pis’ma Zh. Eksp. Teor. Fiz. **76**, 788 (2002) [JETP Lett. **76**, 664 (2002)].
7. I. A. Trojan, M. Eremets, A. G. Gavriliuk, and I. S. Lyubutin, Pis’ma Zh. Eksp. Teor. Fiz. **78**, 16 (2003) [JETP Lett. **78**, 13 (2003)].
8. A. G. Gavriliuk, I. A. Trojan, R. Boehler, and I. S. Lyubutin, Pis’ma Zh. Eksp. Teor. Fiz. **75**, 25 (2002) [JETP Lett. **75**, 23 (2002)].
9. S. G. Ovchinnikov and V. N. Zabluda, Zh. Eksp. Teor. Fiz. **125**, 150 (2004) [JETP **98**, 135 (2004)].
10. S. G. Ovchinnikov, Zh. Eksp. Teor. Fiz. **134**, 172 (2008) [JETP **107**, 140 (2008)].
11. N. B. Ivanova, N. V. Kazak, V. V. Markov, et al., Fiz. Tverd. Tela **46**, 1422 (2004) [Phys. Solid State **46**, 1462 (2004)].
12. N. V. Kazak, A. M. Potseluyko, S. G. Ovchinnikov, and V. A. Chernov, J. Magn. Magn. Mater. **300**, 507 (2006).
13. N. V. Kazak, A. M. Potseluyko, S. G. Ovchinnikov, et al., Physica B **378–380**, 327 (2006).
14. N. B. Ivanova, V. V. Rudenko, A. D. Balaev, et al., Zh. Eksp. Teor. Fiz. **121**, 354 (2002) [JETP **94**, 299 (2002)].
15. I. S. Edelman, A. V. Malakhovsky, T. I. Vasil’eva, and V. N. Seleznev, Fiz. Tverd. Tela **14**, 2810 (1972) [Sov. Phys. Solid State **14**, 2442 (1972)].
16. A. V. Postnikov, St. Bartkowski, M. Neumann, et al., Phys. Rev. B **50**, 14849 (1994).
17. A. G. Gavriliuk, I. A. Trojan, I. S. Lyubutin, et al., Pis’ma Zh. Eksp. Teor. Fiz. **77**, 747 (2003) [JETP Lett. **77**, 619 (2003)].
18. Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 753 (1951).
19. D. T. Sviridov, R. K. Sviridova, and Yu. F. Smirnov, *Optical Spectra of Transition-Metal Ions in Crystals* (Nauka, Moscow, 1976) [in Russian].

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