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# Electronic properties of $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ at ambient conditions and at high pressure

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## Abstract

We present the results of an in-plane resistivity study of the solid solutions  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ . The measurements were made on single crystals with concentration  $x = 0.02, 0.13, 0.18, 0.3, 0.95, 1.0$  in the temperature range 220–600 K. Semiconducting behaviour for samples with  $x \geq 0.13$  was found. Mott variable-range-hopping transport  $\rho(T) = \rho_0 \exp(T^*/T)^\alpha$  has been observed with  $\alpha = 1/4$  at  $T < 290$  K, suggesting carrier localization. Above this temperature the activation-type conductivity, with activation energies,  $E_a$ , about 1 eV for all samples, is observed. The possible electronic states and band structure of  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  crystals are discussed in the different pressure ranges:  $P < P_c^{\text{Fe}}$ ,  $P_c^{\text{Fe}} < P < P_c^{\text{V}}$ ,  $P > P_c^{\text{V}}$ , where  $P_c^{\text{Fe}}$ ,  $P_c^{\text{V}}$  are the critical pressure values for  $\text{FeBO}_3$  and  $\text{VBO}_3$ , respectively.

## 1. Introduction

Since the discovery of high temperature superconductivity in doped cuprate oxides and colossal magnetoresistance in manganite perovskites the electronic and magnetic properties of transition metal oxides has attracted renewed attention. It is believed that the correlation effects among the transition metal 3d electrons and the hybridization between these 3d states and the oxygen 2p states play an essential role in determining the nature of the insulator gap. Using as general guideline a strong electron correlation we search for magnetic oxide materials containing transition elements with new interesting properties. This search led us to synthesize a family of mixed borates  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ .

Green  $\text{FeBO}_3$  is one of the few room temperature ferrimagnetic materials which are transparent well into the visible range. The compound has rhombohedral calcite structure with space group  $R\bar{3}c-D_{3d}^6$  [1]. The canted antiferromagnetic behaviour of  $\text{FeBO}_3$  ( $T_N = 348$  K) is

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due to a slight deviation of the  $\text{Fe}^{3+}$  magnetic moments from a collinear antiparallel alignment within the hexagonal (001) plane [2]. The magnetic hard axis [111] anisotropy field is 3.13 kOe [3], while the in-plane anisotropy field is of the order of 1 Oe [2]. This combination of interesting properties in conjunction with a large Faraday rotation of  $2300^\circ \text{cm}^{-1}$  at  $\lambda = 5250 \text{ \AA}$  makes  $\text{FeBO}_3$  a promising candidate for high-speed magneto-optical applications [4]. The other noteworthy feature for  $\text{FeBO}_3$  is that it has a single Fe site and therefore gives a simple Mössbauer spectrum [5–7].

At ambient conditions  $\text{FeBO}_3$  is an insulator with a band gap about 2.9 eV obtained from the onset of the fundamental optical absorption edge [8]. Recently the transition from a magnetic to a non-magnetic state at a pressure of about 46 GPa in single crystals [9] and a structural transition at 52 GPa in powders [10] of  $\text{FeBO}_3$  have been discovered. The magnetic property changes are explained by the high spin (HS)–low spin (LS) crossover [11].

Although iron borate has been extensively investigated for many years, little is known about  $\text{FeBO}_3$  solid solutions. A small number of compositions including transition metal ions have been synthesized and studied, e.g.  $\text{Fe}_{1-x}\text{Cr}_x\text{BO}_3$ ,  $\text{Fe}_{1-x}\text{Mn}_x\text{BO}_3$  [12].

In this paper we present the results of resistivity measurements at ambient conditions and predictions of band structure changes in the high-pressure phase of mixed borate  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ . The choice of  $\text{V}^{3+}$  as substituted ion was dictated by different magnetic and electrical properties of the end compounds:  $\text{VBO}_3$  is a ferromagnet ( $T_C = 32 \text{ K}$ ) and a semiconductor [13].

## 2. Experimental procedure

The single crystals of  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  that are studied here are the same as those described in [14], where a detailed discussion of the preparation is given. The ionic radii of  $\text{V}^{3+}$  and  $\text{Fe}^{3+}$  ions are close, which allows us to grow  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  samples with composition  $x = 0.02, 0.13, 0.18, 0.3, 0.95$ . The elemental composition of the grown samples was determined by energy-dispersive x-ray spectroscopy (EDAX ZAF quantification procedure). The x-ray diffraction was studied on a setup of the D8 ADVANCE type using Cu  $K\alpha$  radiation ( $\lambda = 1.506 \text{ \AA}$ ). The cell parameters for  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  solid solutions are in accordance with the known ionic radii.

The dc resistivity measurements were performed in the temperature range from 600 to 220 K, below which the resistance was too large to be measured accurately. Due to high resistances we used a two-probe scheme of the measurements. Low contact resistance of a few ohms is achieved by soldering thin copper wires with indium–silver alloy onto the crystals.

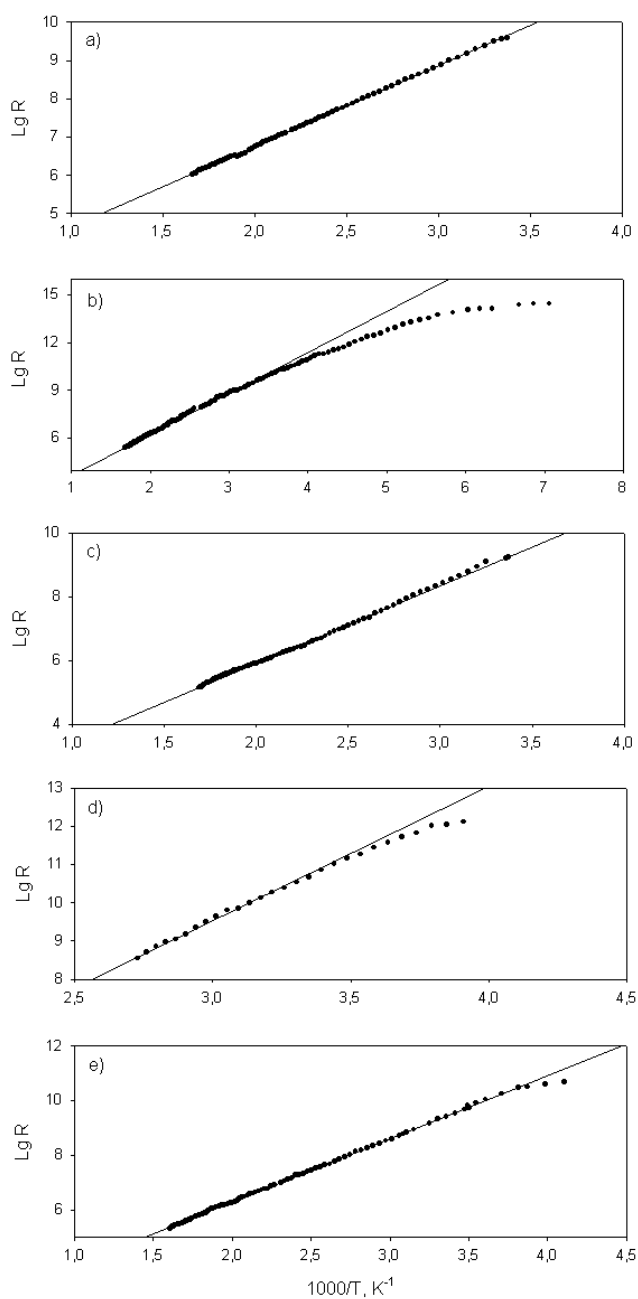
## 3. Resistivity measurements of $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$

In figure 1 the in-plane resistivity as a function of the inverse temperature on a  $\log_{10} R$  scale for different  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  single crystals is shown. All samples show semiconducting behaviour except for crystals with low vanadium content  $x = 0.02$ , which are insulators just as  $\text{FeBO}_3$ .

The resistivity is proportional to  $\exp(E_a/kT)$  at  $T > 290 \text{ K}$ , and the estimated activation energies  $E_a$  are about 1 eV for all the samples, as can be seen from table 1. The resistivity in the insulating phase is expected to exhibit variable-range hopping (VRH) at low temperatures of the form

$$\rho(T) = \rho_0 \exp\left(\frac{T^*}{T}\right)^\alpha, \quad (1)$$

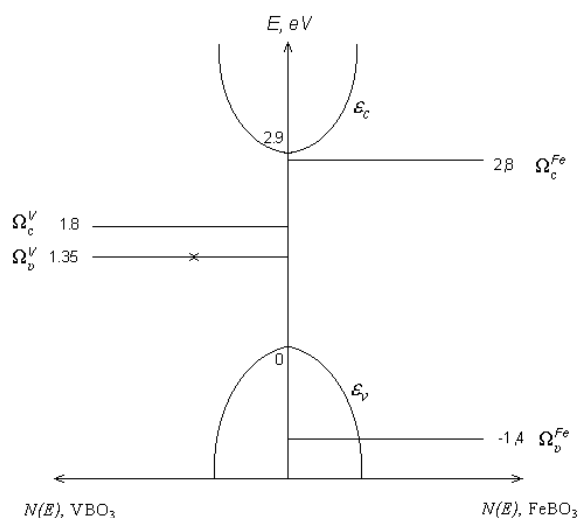
where  $\alpha = 1/(d + 1)$  and  $d$  is the dimensionality of the system, assuming that the density of states  $N(\epsilon_F)$  at the Fermi level is finite. The parameter  $T^*$  is related to  $N(\epsilon_F)$  and the localization length  $\xi$ . The temperature dependence of  $\rho_0$  is generally weak and can be neglected. It is



**Figure 1.** The resistivity as function of  $T^{-1}$  on a logarithmic scale for (a)  $\text{Fe}_{0.87}\text{V}_{0.13}\text{BO}_3$ , (b)  $\text{Fe}_{0.82}\text{V}_{0.18}\text{BO}_3$ , (c)  $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$ , (d)  $\text{Fe}_{0.05}\text{V}_{0.95}\text{BO}_3$ , (e)  $\text{VBO}_3$ .

found that strong electron interactions yield a hopping exponent  $1/2$  while weak interactions (compared with hopping energies) give rise to an exponent  $1/4$ .

Fitting with  $\alpha = 1/4$  gave satisfactory results for  $x = 0.13, 0.18, 0.3$  and  $0.95$  at  $T < 290$  K. In  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  solid solutions V substitution would bring a random potential,



**Figure 2.** Scheme of the  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  density of states:  $\text{VBO}_3$ —left insert,  $\text{FeBO}_3$ —right insert.

**Table 1.** Activation energies for solid solutions  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ .

$\text{Fe}_{1-x}\text{V}_x\text{BO}_3$	$E_a$ (eV)
$\text{Fe}_{0.87}\text{V}_{0.13}\text{BO}_3$	0.88
$\text{Fe}_{0.82}\text{V}_{0.18}\text{BO}_3$	1.02
$\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$	0.96
$\text{Fe}_{0.05}\text{V}_{0.95}\text{BO}_3$	0.94
$\text{VBO}_3$	0.92

that could localize the itinerant electrons. Thus,  $\alpha = 1/4$  indicates that the localization of the charge carriers has occurred and the conduction mechanism has changed from simple activated type to a three-dimensional VRH as the temperature is decreased.

The value  $\alpha = 1/4$  proves the weak interaction of the carriers. This may happen in a Mott–Hubbard insulator if superconductivity at low temperatures takes place in the impurity band, near the top of the oxygen valence band. The electronic structures of the end members  $\text{FeBO}_3$  and  $\text{VBO}_3$  are determined by strong electron correlations. For  $\text{FeBO}_3$  the lower Hubbard band (LHB)  $\Omega_v$  ( $d^4 \rightarrow d^5$  excitations) and the upper Hubbard band (UHB)  $\Omega_c$  ( $d^5 \rightarrow d^6$  excitations) are shown in the right-hand side of figure 2. Thus  $\text{FeBO}_3$  is a charge-transfer insulator. In  $\text{VBO}_3$  the LHB  $\Omega_v$  is formed by  $d^1 \rightarrow d^2$  excitations and the UHB  $\Omega_c$  corresponds to  $d^2 \rightarrow d^3$  excitations. The different multi-electron contributions to  $U_{\text{eff}} = \Omega_c - \Omega_v$  for  $\text{V}^{3+}$  and  $\text{Fe}^{3+}$  ions result in a smaller value of  $U_{\text{eff}}$  for  $\text{VBO}_3$ , and in the Mott–Hubbard nature of the gap (left-hand side of figure 2) [15]. For solid solutions  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  the energy scheme is given by the superposition of both sides in figure 2.

For  $\text{VBO}_3$ , the  $\Omega_v$  and  $\Omega_c$  levels are localized and could not make a contribution to conductivity; therefore, the value of  $2E_a$  can be assumed to be an energy of charge transfer excitation  $p^6d^2 \rightarrow p^5d^3$ . This process gives rise to the appearance of the holes on the oxygen at the top of the valence band, and to a change of the valence state of vanadium to  $\text{V}^{2+}$ . One could suppose that the high temperature conductance in this borate is accomplished by holes in broad valence band. As can be seen from figure 2, the unoccupied upper d-band of vanadium

( $\Omega_c^V = 1.8$  eV) is situated much lower than that for iron ( $\Omega_c^{\text{Fe}} = 2.8$  eV). Because the activation energies  $E_a$  for all semiconducting samples have close values it is possible that the mechanism of conductivity in  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  solid solutions has the same origin as in  $\text{VBO}_3$ .

#### 4. Prediction of $\text{VBO}_3$ and $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ band structure at high pressure

Recent experiments on  $\text{FeBO}_3$  have shown non-trivial changes of the magnetic, electronic and optical properties under high pressure. These have been explained by crossover of the high-spin ( $S = 5/2$ ) $d^5$  and low-spin ( $S = 1/2$ ) $d^5$  terms as the crystal field parameter  $\Delta$  is increased [16].

A similar analysis of the Tanabe–Sugano diagrams for  $d^1$ ,  $d^2$ , and  $d^3$  configurations reveals no crossover of the high-spin and the low-spin terms with increasing  $\Delta$ . Moreover, the value of  $U_{\text{eff}}$  for  $\text{VBO}_3$  does not depend on  $\Delta$  [15]. For  $\text{VBO}_3$  we expect a Mott transition at high pressure, when the insulator gap  $E_g = U_{\text{eff}} - 12t$  goes to zero due to the increase in the effective V–V hopping parameter  $t$ . Here  $t$  is formed by the weak V–O $\pi$ -bonding and is assumed to be much smaller than  $t$  in  $\text{FeBO}_3$  ( $\sigma$ -bonding). Due to the close Fe–O and V–O distances we suppose  $\partial t/\partial P$  in  $\text{VBO}_3$  to be the same as in  $\text{FeBO}_3$ :  $\partial t/\partial P = 0.00046$  eV GPa $^{-1}$ . The critical pressure  $P_c^V$  is given by

$$P_c^V = \frac{U_{\text{eff}} - 12t(p=0)}{12 \frac{\partial t}{\partial P}}. \quad (2)$$

Using  $U_{\text{eff}} = 0.45$  eV [15] and  $t(P=0) = 0.01$  eV (the larger  $t_\sigma$  for  $\text{FeBO}_3$  was estimated to be 0.05 eV [16]) one obtains  $P_c^V = 60$  GPa for  $\text{VBO}_3$ . The main uncertainty comes from the  $t(P=0)$  value. Even 100% deviation  $t = 0.01 \pm 0.01$  eV results in smaller deviation for  $P_c^V = 60 \pm 20$  GPa.

Taking into account the value of the critical pressure for  $\text{FeBO}_3$   $P_c^{\text{Fe}} = 46$  GPa, for solid solutions  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ , three different regions of the pressure can be distinguished:

- (i)  $P < P_c^{\text{Fe}}$ , an insulator with a mixture of  $\text{Fe}^{3+}$  ( $S = 5/2$ ) and  $\text{V}^{3+}$  ( $S = 1$ ) ions;
- (ii)  $P_c^{\text{Fe}} < P < P_c^V$ , an insulator with a mixture of  $\text{Fe}^{3+}$  ( $S = 1/2$ ) and  $\text{V}^{3+}$  ( $S = 1$ ) ions;
- (iii)  $P > P_c^V$ , a mixture of the conducting nonmagnetic and the nonconducting magnetic regions.

Finally, at  $P \approx 200$  GPa when  $\text{FeBO}_3$  is expected to become metallic [16], the  $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$  crystals will also become metallic and nonmagnetic.

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