

Electron Transport in FeBO₃ Ferroborate at Ultrahigh Pressures

I. A. Troyan^{a,b}, A. G. Gavrilyuk^{a,c}, S. G. Ovchinnikov^{d,e}, I. S. Lyubutin^a, and N. V. Kazak^d

^a Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119333 Russia

^b Max-Planck Institut für Chemie, Mainz, 55020 Germany

^c Institute for Nuclear Research, Russian Academy of Sciences, Troitsk, Moscow region, 142190 Russia

^d Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

^e Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660041 Russia

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The electrical resistance of FeBO₃ crystals at high and ultrahigh pressures (up to 198 GPa) and low temperatures has been measured using diamond anvil cells. It has found that in the high-pressure phase, 46 GPa < P < 100 GPa, the activation energy E_{ac} decreases gradually from 0.55 to 0.3 eV according to a linear law. Its extrapolation to zero gives an estimated value of about 210 GPa for the pressure at which complete metallization is expected. However, above 100 GPa, the linear $E_{ac}(P)$ dependence smoothly transforms to a nonlinear one. At the same time, the temperature dependence of the electrical resistance at fixed pressure significantly deviates from the Arrhenius activation law and does not obey the Mott law for the hopping conductivity. Experimental data demonstrate the dependence of the activation energy E_{ac} both on pressure and temperature. At $T = 0$, the gap tends to zero. Theoretical analysis shows that the decrease in E_{ac} upon cooling can be interpreted in terms of the transition of the low-spin FeBO₃ phase to the magnetically ordered (antiferromagnetic) state.

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1. INTRODUCTION

Iron borate FeBO₃ is a rare material that is transparent in the optical range and has a spontaneous magnetization at room temperature. The FeBO₃ crystal has the rhombohedral calcite structure [1]. Under ambient conditions, it is an antiferromagnet with weak ferromagnetism [2] and its Néel temperature is about 348 K [3]. At ambient pressure, iron borate is an insulator with an optical gap of 2.9 eV [4]. In terms of electronic properties, FeBO₃ is a typical example of strongly correlated electron systems [5–8]. Depending on the ratio of the energy U of the onsite Coulomb repulsion ($d-d$ gap) and the charge transfer energy Δ ($p-d$ gap), such materials can be either Mott insulators [5–7] or charge-transfer insulators [8–10]. At high pressure, these systems can exhibit an insulator–metal transition accompanied by an abrupt change in the magnetic and optical properties [9, 11].

In our earlier high-pressure studies of iron borate, we have observed the collapse of magnetization at $P \approx 46$ GPa (at room temperature) [12, 13] and the structural phase transition at about 53 GPa accompanied by a stepwise change in the unit cell volume by about 9% [14]. The corresponding ⁵⁷Fe Mössbauer spectra suggest the abrupt change in the electronic properties at

$P \approx 46$ GPa, in particular, the spin-state transition for Fe³⁺ ions from the high-spin (HS, $S = 5/2$) to the low-spin (LS, $S = 1/2$) state [13]. The HS–LS crossover is accompanied by the electron transition of the insulator–semiconductor type with a drop in the optical gap from 3 to 0.75 eV [15–17]. With a further increase in pressure up to 80 GPa [16], the optical gap changes only slightly and the activation energy decreases from 0.55 eV at 70 GPa to 0.2 eV at 140 GPa. However, the problem of complete metallization remains unsolved.

In this work, we directly measure the electrical resistivity for the FeBO₃ crystal at high and ultrahigh pressures up to about 200 GPa (2 Mbar) in a diamond anvil cell. At different pressures, the temperature dependence of the electrical resistance has been measured in the 4.2–300 K (or 77–300 K) range.

2. EXPERIMENTAL TECHNIQUE

The resistivity measurements in the diamond anvil cell [18] were performed using a special facility available in the High-Pressure Group of the Max Planck Institute (Mainz, Germany). For the measurements, we use a composite boron nitride gasket and contacts made of platinum foil. The photomicrograph of the experimental assembly is shown in Fig. 1. The signals

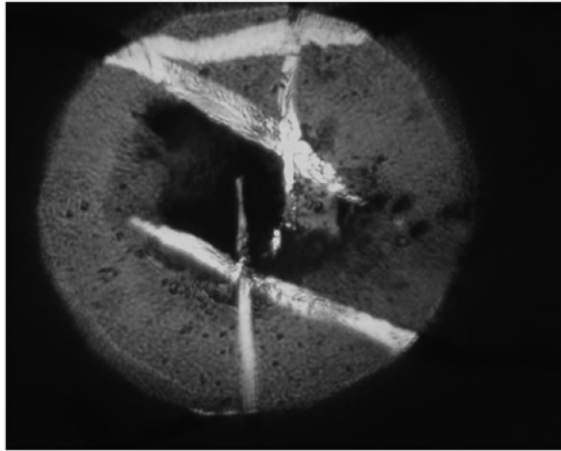


Fig. 1. Micrograph of the experimental assembly for measuring electrical resistance of the FeBO₃ crystal by the quasi-four-probe method. The diameter of the working area is about 100 μm .

were measured by a two-channel PerkinElmer DSP Lock-in 7265 detector according to the quasi-four-probe technique. The accuracy of temperature measurements was 0.1 K in the entire 4.2–300 K range.

When the high-pressure cell was installed in a cryostat and connected to the measuring system, it was found that the leakage current for the sample in the insulating state (at $P = 10$ GPa) was 0.5 pA. Therefore, the actual accuracy for measurements of electrical resistance R was determined in our experiment by the driving voltage generator. The measurements were performed at a low driving voltage (0.01 V) with an accuracy of 10 μV , which corresponds to an experimental error of 0.1%.

In our experiment, we used flat anvils 100 μm in diameter (see Fig. 1). The single-crystalline FeBO₃ plate with a thickness of about 4 μm and a characteristic in-plane size of about 35 μm was placed in the center of the working volume of the boron nitride gasket. The basal (111) plane of the plate was parallel to the plane of the diamond anvils. We did not use any additional pressure transmitting medium. To measure the pressure (according to the ruby reference scale), micrometer-size ruby crumbs were distributed over the working volume of the cell. The pressure scatter over the sample resulting from the nonhydrostatic conditions was 3 GPa between the two nearest electrodes at a pressure level of 100 GPa. This value was assumed to be the experimental error for pressure measurements.

In the course of our measurements, the pressure in the cell was measured and fixed at room temperature. Then, the cell connected to the measuring system was placed into the continuous-flow helium cryostat. The temperature sensor was attached to the case of the cell. The cell was cooled down to 77 K for 3 h. At each fixed pressure value, the measurements of the electrical resistance as a function of temperature were per-

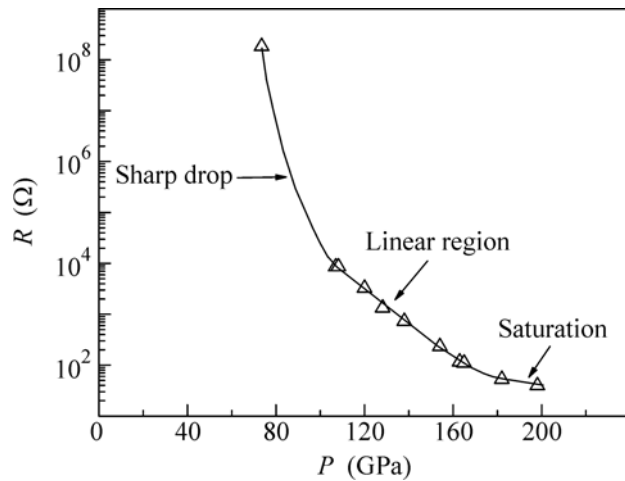


Fig. 2. Pressure dependence of the electrical resistance for the FeBO₃ crystal at room temperature (300 K).

formed on heating for 8 h. The pressure was measured before and after the temperature run. In the course of numerous experiments, it was found that the pressure in this cell increases upon cooling and does not return to the initial value upon heating. Therefore, in our experiments discussed here, the pressure on the sample was also assumed to be equal to that measured after heating of the cell.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The electrical resistance of FeBO₃ was studied at pressures of up to 198 GPa. At each fixed pressure, we measured the temperature dependence of the resistance in the 77–300 K (or 4.2–300 K) range to determine the type of conductivity (metallic or semiconducting) and to calculate the activation energy in the case of nonmetallic conductivity.

At pressures $P < 46$ GPa, the sample remained in the high-resistivity state and the electrical resistance of FeBO₃ becomes measurable only in the high-pressure phase at $P > 46$ GPa after the electron transition of Fe³⁺ ions to the low-spin state. Figure 2 shows the pressure dependence of the electrical resistance at room temperature. In this dependence, we can identify three characteristic regions: (1) the region of the steep decrease in resistance (the decrease is significantly faster than that according to the exponential law), which is observed just after the insulator–semiconductor transition (in the 46–100 GPa pressure range); (2) the region of the uniform exponential decrease in the resistance (100–160 GPa); and (3) the “saturation” region where the rate of the resistance decrease abruptly slows down (160–198 GPa). At room temperature, the crystal remains in the semicon-

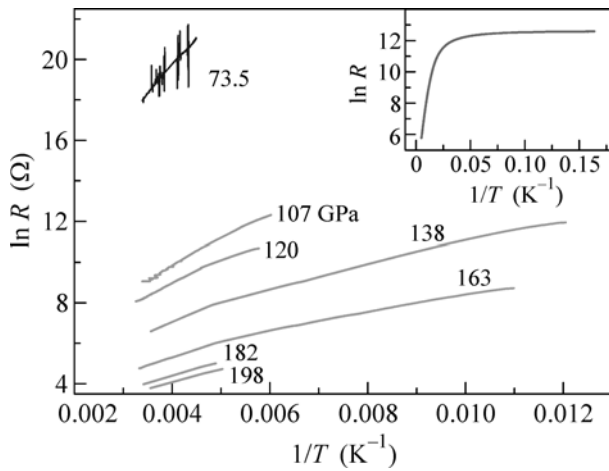


Fig. 3. Evolution of the temperature dependence of the electrical resistance for the FeBO_3 crystal with the growth of pressure. The plot of $\ln R$ versus the inverse temperature at 163 GPa for the whole temperature range down to the liquid helium temperature is shown in the inset.

ducting phase and the transition to the metallic state is not observed.

Figure 3 shows the dependence of R (in the logarithmic scale) on the inverse temperature at different pressures. It is clear that the type of this dependence is characteristic of the semiconducting state. Up to pressures on the order of 100 GPa, this dependence is well described by the Arrhenius formula

$$R = R_0 \exp(E_{ac}/kT). \quad (1)$$

Hence, we can determine the activation energy E_{ac} for the conductivity.

At pressures exceeding 100 GPa, this dependence at low temperatures more and more deviates from (1). Especially clear illustration is given in the inset of Fig. 3, where we show the $\ln R(1/T)$ plot based on the measurements down to liquid helium temperatures at 163 GPa. The strong nonlinearity at low temperatures is clearly pronounced.

The values of the thermal activation energy for the conductivity calculated in the vicinity of room temperature at different pressures are given in Fig. 4. Just after the electron transition at $P = 46$ GPa, the activation energy E_{ac} is equal to 0.55 eV. In the high-pressure phase within the $46 \text{ GPa} < P < 100 \text{ GPa}$ range, E_{ac} decreases steeply down to about 0.2 eV. Within the 100–160 GPa pressure range, $E_{ac}(P)$ curve has a nearly linear form. Above 160 GPa, the slope of the pressure dependence decreases significantly and the $E_{ac}(P)$ curve flattens.

The presented data suggest that the pressure corresponding to the complete metallization of the FeBO_3 crystal far exceeds the value of 210 GPa [13] found earlier by the linear extrapolation of experimental $E_{ac}(P)$ plots obtained at lower pressures. Instead of the

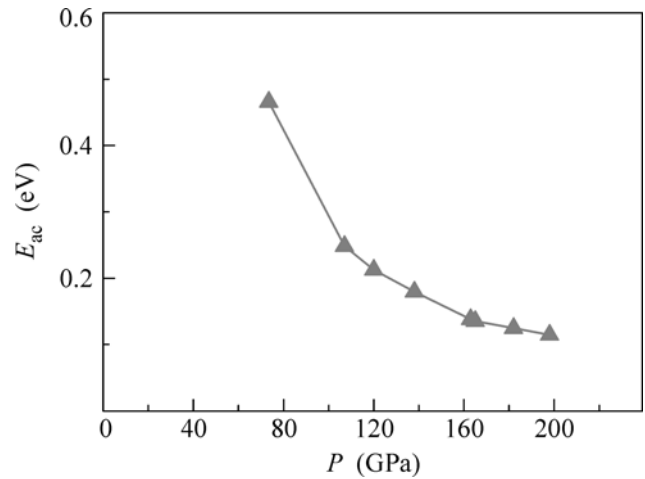


Fig. 4. Pressure dependence of the activation energy for the FeBO_3 crystal calculated near room temperature (300 K).

metallization expected at about 2 Mbar, the FeBO_3 crystal passes to an anomalous narrow-gap semiconducting state characterized by a weak pressure dependence of the activation gap and by an appreciable deviation of the $R(T)$ dependence from the Arrhenius law in the low-temperature range.

At the same time, if we assume that the Arrhenius law is valid, it follows from experiment that the activation energy E_{ac} should be temperature dependent. Under this assumption, we calculated the temperature dependence $E_{ac}(T)$ of the activation energy based on the experimental data at $P = 138$ and 163 GPa (Fig. 5). In Fig. 5, we can see that E_{ac} at 163 GPa does not change upon cooling down to about 100 K; with the further cooling, it decreases steeply and tends to zero at $T \rightarrow 0$. The analysis of possible mechanisms of the insulator–metal transition [19] did not reveal such a behavior in any earlier known case.

4. DISCUSSION AND THEORETICAL ANALYSIS OF THE RESULTS

The decrease in E_{ac} upon cooling seems to be related to the arising magnetic ordering in the low-spin system of Fe^{3+} ions ($S = 1/2$). In earlier experiment [20] at pressures exceeding the critical value ($P > P_c = 46 \text{ GPa}$), we observed magnetic correlations in the FeBO_3 crystal at low temperatures (with $T_N \approx 50 \text{ K}$ at $P = 49 \text{ GPa}$). The value of T_N grows with pressure. At pressures below and above the HS–LS crossover, the magnetic behavior of FeBO_3 borate (both in the HS and LS states) was analyzed in detail in [20]. In the table, we present the expected values of the Néel temperature, calculated using Eq. (10) from [20]. The arrows in Fig. 5 indicate the expected theoretical val-

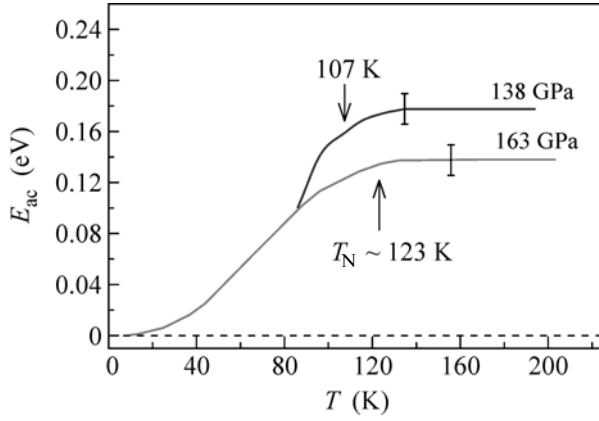


Fig. 5. Temperature dependence of the activation energy for the FeBO₃ crystal calculated from the experimental data for the temperature dependence of the electrical resistance at pressures of 138 and 163 GPa. The calculations were performed under assumption of the validity of the Arrhenius law with the variable activation energy. The arrows indicate the calculated values of the Néel temperature at these pressures for the low-spin state of Fe³⁺ ions in the FeBO₃ crystal. Error bars indicate the statistical error for E_{ac} .

ues for T_N at 138 and 165 GPa. We can see that the anomalies in the experimental $E_{ac}(T)$ curves correlate well with the presupposed magnetic ordering at these temperatures.

Our earlier analysis [20] of the P – T phase diagram for the FeBO₃ crystal demonstrated that as the d level approaches the top of the valence band formed by oxygen p states, the situation corresponds to the Kondo lattice. In this case, the most adequate is the Anderson model with the hybridization of p and d electrons rather than the multiband Hubbard model. At pressures far below the critical value P_{c2} (see below), when the d level is far from the top of the valence p band, the contribution of the hybridization effects is negligibly small and the multiband Hubbard model works well. However, the hybridization is rather important near the expected metallization.

In the general case, the insulating gap E_g is determined by the difference between the energies (E^+ and E^-) of the hybridized bands

$$E^{\pm} = [\varepsilon_d + \varepsilon_v \pm \sqrt{(\varepsilon_d - \varepsilon_v)^2 + \tilde{V}_{pd}^2}]/2, \quad (2)$$

$$E_g = E^+ - E^- = \sqrt{(\varepsilon_d - \varepsilon_v)^2 + \tilde{V}_{pd}^2},$$

Theoretical values of T_N at different pressures P for the low-spin state ($S = 1/2$) of Fe³⁺ ions in the FeBO₃ crystal, calculated according to Eq. (10) from [20]

P	46	107	120	138	163	165	182	198
T_N	51	88	96	107	123	124	134	144

where ε_d is the energy corresponding to the bottom of the d band, ε_v is the energy of the top of the valence band, and \tilde{V}_{pd} is the energy of the hybridization between d states of the transition metal and oxygen p states. There is a critical pressure P_{c2} at which the narrow d band could intersect with the top of the valence band in the absence of the hybridization. At $P < P_{c2}$, the hybridization is small and the condition $\varepsilon_d - \varepsilon_v \gg \tilde{V}_{pd}$ is met, that is,

$$E_g = \varepsilon_d - \varepsilon_v. \quad (3)$$

In the vicinity of the transition, where $\varepsilon_d \rightarrow \varepsilon_v$, the band gap is $E_g = |P = P_{c2}, \varepsilon_d = \varepsilon_v| \rightarrow \tilde{V}_{pd}$. This is the hybridization gap in the paramagnetic state.

In the magnetically ordered state, the effects of strong correlations lead to renormalization of the hybridization parameter in such a way that it becomes dependent on the magnetic order parameter. Such a renormalization was first determined for magnetic semiconductors in the ferromagnetic phase [21] and then also for the antiferromagnetic state [22]. It was shown that the hybridization becomes spin-dependent and vanishes at zero temperature for one of the spin components (in the case of an antiferromagnet), namely,

$$\tilde{V}_{pd} = V_{pd}(1 - \langle S_A^z \rangle / S), \quad (4)$$

where $\langle S_A^z \rangle$ is the z component of the average spin for one sublattice (sublattice A) and S is the total spin. The magnetization of each sublattice vanishes at T_N .

At $T \rightarrow 0$, the average spin becomes equal to its nominal value (neglecting the small contribution of zero-point quantum vibrations) and gap (4) vanishes.

Probably, this novel metallization mechanism could be relevant to the experimental results reported in this paper. At ultrahigh pressures, the abrupt drop in the activation energy E_{ac} beginning below T_N agrees well with the theoretical predictions.

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