Electrical conductivity measurements of β-boron under high pressure and temperature

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Abstract

Using a microcircuit fabricated on a diamond anvil cell, we carried out *in situ* conductivity measurements on β-boron at pressures up to 28 GPa. The electrical conductivity of the sample increases with increasing pressure, but it does not return to original state when the pressure returns to ambient. As the conductivity gradually increases within a temperature region from 293 to 473 K, two significant different conduction processes are observed. A possible reason for this result is proposed based on the valence band structure. In addition, by laser heating, our experimental result indicates that β-boron still shows the transport behavior of a semiconductor.

1. Introduction

Boron has various physical properties due to its unusual chemical bonding and very complex crystal structure. Boron also occupies an important place in the field of materials science. It has technologically interesting properties such as a high melting point, extreme hardness and high resistance to chemical attacks. Boron is distinct from other semiconductor materials, since an icosahedral cluster of 12 boron atoms is a common structure unit, which essentially determines the crystal and electronic structures of boron-rich solids. This basic B_{12} unit forms many complex polymorphs of boron [1]. β-boron is the most universal and stable form. However, the B_{12} cluster is not stable itself, so it is not a molecular crystal [2]. The structural formula of β-boron is $(B_{12})_4(B_{28})_2B$ or $B_{84}(B_{10})_2B$, and each cell contains 105 boron atoms. Its crystal structure has rhombohedral symmetry [3]. Schmechel *et al* described the energy band diagram of a separation of occupied and unoccupied electronic states, which is caused
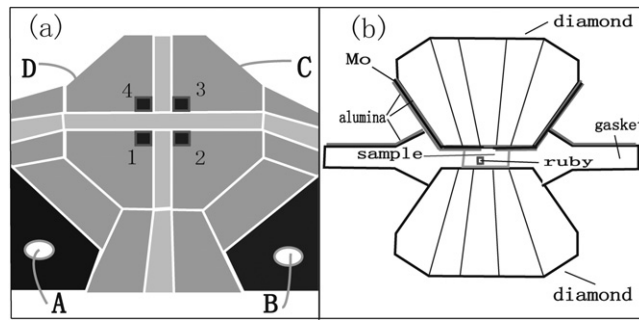
Figure 1. (a) Configuration of a microcircuit on a diamond anvil. 1, 2, 3, and 4 denote exposed Mo electrodes (four small black squares region); A, B, C, and D denote the four contact ends of the microcircuit. (b) Diagram of a microcircuit in a diamond anvil cell at its working conditions.

by the distorted icosahedra at the vertex of the unit cell due to the Jahn–Teller effect [4]. Depending on temperature and preceding optical excitation or other conditions of measurement, a superposition of hopping conductivity and band type conductivity occurs [5]. Based on the actual conditions, one of these mechanisms may predominate. In most cases, however, it is difficult to elucidate the transport mechanisms on the specific condition.

The abundant electric property, for example switching effect, variable-range hopping in the low-field and non-ohmic electrical conductivity in high electric fields, of β-boron is extensively investigated at ambient pressure [6–9]. But many previous studies of boron at high pressure have concentrated on structural characterization [10–12]. The conductive properties under high pressure have rarely been reported, due to boron's high resistance. Only Eremets *et al* has reported that β-boron had been found to transform from a nonmetal to a superconductor at 160 GPa [13]. However, many details related to the conductivity under high pressure still remain unknown. We have carried out *in situ* conductivity measurements of β-boron to investigate the possible conductivity variation and to find its conduction mechanism under high pressure, to better understand the temperature dependence of the electrical conductivity in some special pressure–temperature (P–T) regions.

2. Experimental details

A Mao–Bell-type diamond anvil cell (DAC) was used in our experiment; the facet diameter of the diamond anvil was 400 μm. T-301 stainless steel was used as a gasket, pre-indented to 50 μm thickness. A hole of 150 μm diameter was drilled in the middle of the gasket, and 2 μm of alumina was sputtered on the gasket for insulation. A high-purity boron sample (99.9999%) was used. No pressure medium was loaded in order to avoid the introduction of impurities for measurement of resistivity and to ensure good electrical contact. The ruby fluorescence method was used for pressure calibration. We chose molybdenum (Mo) as the electrode and alumina as the protecting and adiabatic layer, respectively. The manufacturing process was similar to that described in previous works [14–17]. The final microcircuit is shown in figure 1(a). Figure 1(b) shows a schematic diagram of a sample arranged in the DAC.

In our experiments, a Nd:YLF laser was used to heat the sample from 1575 to 2224 K. The maximum laser power is 48 W. A thermoelectrically cooled charge-coupled device (CCD) detector equipped with an Acton SpectraPro300i spectrograph was used for the temperature measurement. The alumina film deposited on the faces of diamond composed a chamber of
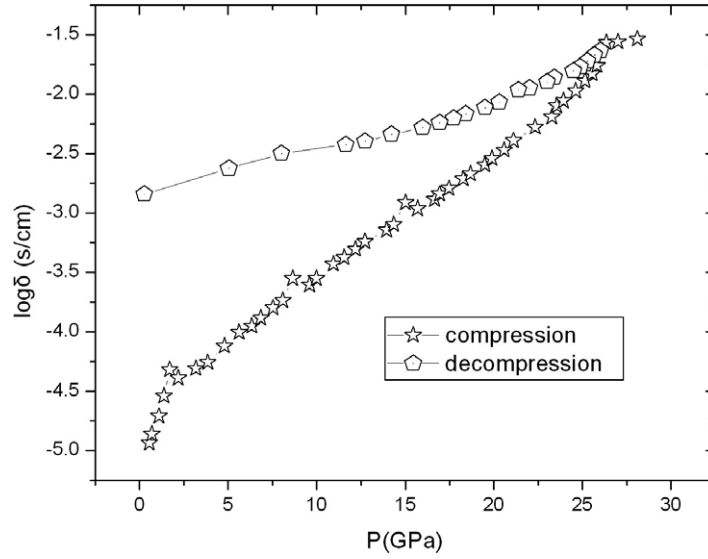
Figure 2. The plot of electrical conductivity versus pressure of β-boron, to 28 GPa.

heat preservation, which was an effective method to prevent loss of heat. So *in situ* resistance measurement can be performed at high pressure and high temperature (HTHP).

The van der Pauw method, with the following formula, was utilized to calculate the conductivity of the sample:

$$\exp(-\pi L R_1 \sigma) + \exp(-\pi L R_2 \sigma) = 1, \tag{1}$$

where $R_1 = V_1/I_1$, $R_2 = V_2/I_2$, σ is the electrical conductivity of the sample, and L is the thickness of the sample. The current I_1 is applied across the contacts A and B, and the potential difference V_2 across the contacts C and D is measured; then, the current I_2 is applied across the contacts B and C, and the potential difference V_2 across the contacts A and D is measured. The thickness of the sample under pressure is determined with a modified micrometer.

3. Results and discussions

A plot of the logarithm of the conductivity of β-boron versus pressure is shown in figure 2. Within the accuracy of the measurement, the conductivity is estimated to be not more than $10^{-5} \ \Omega^{-1} \text{cm}^{-1}$ at ambient pressure. With further increasing the pressure to 28 GPa, the electrical conductivity increases smoothly and reaches the order of $10^{-2} \ \Omega^{-1} \text{cm}^{-1}$. Because the electron transport behavior is related to the crystal structure, we believe that abnormal resistance changes reflect the phase transitions of the sample under high pressure. However, the relation of pressure versus logarithm of electrical conductivity is nearly linear in our experiment, except for a small variation at very low pressure, indicating that no phase transition occurs. This is consistent with a report (high-pressure x-ray) by Nieto *et al* [11].

The increasing electrical conductivity is attributed to the electron wavefunction overlaps for a semiconductor with deceasing atomic distance under increasing pressure [18]. After decompression, the electrical conductivity does not return to its original state. We fit the data by $d(\ln \delta)/dP = C$, where C is constant and δ denotes the electrical conductivity of β-boron. It is found that $C = 0.259\,35 \ \text{GPa}^{-1}$ in compression and $C = 0.103\,93 \ \text{GPa}^{-1}$ in decompression.
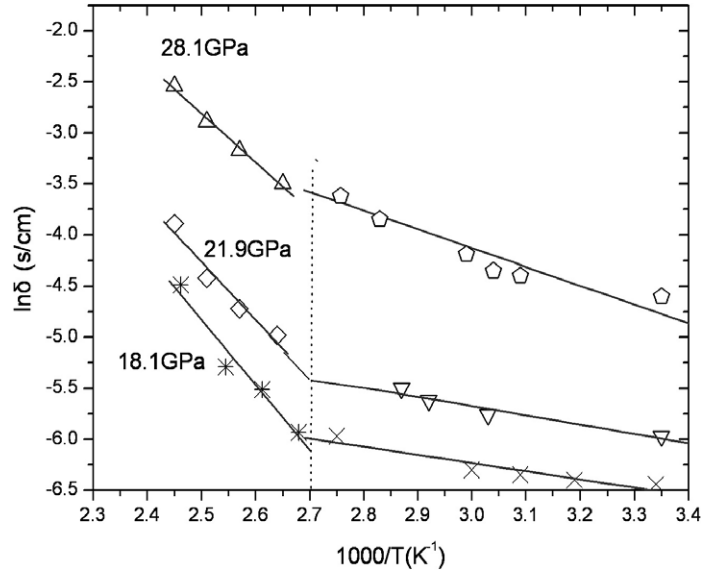
Figure 3. The plots of $\ln \delta$ versus $1000/T$ at 18.1, 21.9 and 28 GPa.

Table 1. Activation energy of β-boron under pressures of 18.1, 21.9 and 28 GPa.

| P (GPa)	298–370 K		370–423 K	
	E (eV)	δ_0 (s cm^{-1})	E (eV)	δ_0 (s cm^{-1})
18.1	6.9×10^{-2}	2.1×10^{-2}	5.4×10^{-1}	6.6×10^4
21.9	7.8×10^{-2}	5.2×10^{-2}	4.8×10^{-1}	1.8×10^4
28	1.5×10^{-1}	3.9	4.1×10^{-1}	8.9×10^3

In general, the electrical conductivity of a semiconductor is determined by the energy band gap at a given temperature, as $\sigma = \sigma_0 \exp(-Eg/2k_{\mathrm{B}}T)$ [19]. So our result indicates that the magnitude of the slope, $\mathrm{d}(Eg)/\mathrm{d}P$, in decompression is smaller than that in compression.

Partial occupancies and vacancies in the crystal structure of β-B are intrinsic structure properties [20]. As the pressure increases, the β-boron crystal will adjust the occupancies and vacancies to adapt to pressure-induced lattice deformation. So some specific and partly occupied states in the band gap, evoked by structural defects, will reflect the change. When the pressure returns to ambient, these changed states cannot return to the original condition. As a result, the total process is not reversible.

Figure 3 shows the electrical conduction of β-boron from room temperature to 423 K at several pressures. We observed two different changes of conductivity with temperature. The changes of conductivity versus temperature become relatively steep after 370 K. From our results, the activation energy of conduction, E, can be obtained by the Arrhenius equation [21, 22]:

$$\sigma = \sigma_0 \exp(-E/kT), \tag{2}$$

where σ is the electrical conductivity, σ_0 is the electrical conductivity at infinitely high temperature, E is the activation energy, and k is the Boltzmann constant. The plot of conductivity versus temperature under fixed pressures can be fitted by two lines. The result is shown in table 1.
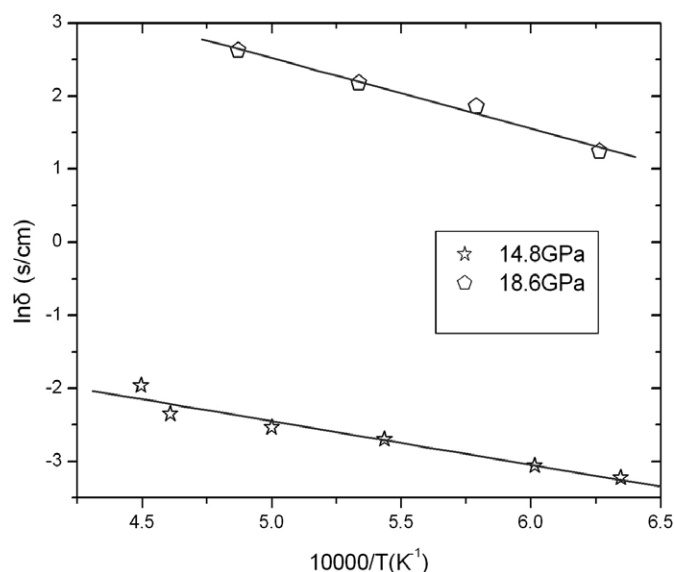
Figure 4. Electrical conductivity of the sample as a function of reciprocal temperature at 14.5 and 18.6 GPa.

It is well known that the valence band is composed of a higher valence band (VB1) and a lower valence band (VB2). VB1 (the energy level is 0.188 eV) consists of localized states, and it is partly filled by electrons coming from other impurity elements [23]. Furthermore, partly occupied states, at about 0.18–0.3 eV in the energy band scheme, are induced by structural defects [24]. Our results show that the activation energy is lower than 0.18 eV in the temperature region 298–370 K. So we think that electrons in VB2 will be excited into the unoccupied sites of VB1 at 298–370 K. This implies that band-type conductivity (the valence electrons are excited into unoccupied gap states) is mainly a transport mechanism. When the temperature is close to 370 K, the number of electrons transiting from VB2 to VB1 reaches a maximum. However, as the temperature continues to increase to 423 K, the electrical conductivity rapidly increases, and the activation energy is larger than 0.3 eV. Here, we assume that VB1 will mainly play the role of an excited state. The activation energy will increase because of there being more activated charge carriers with the effect of temperature at the same pressure. In addition, we find that the inflexion (about at 370 K), which separates two conduction processes, does not change with pressure. It is proposed that this relates to the crystal structure of sample.

As can be seen in figure 4, the electrical conductivity significantly increases in the temperature range 1575–2224 K. The maximum of the conductivity is 10^1 Ω^{-1}cm^{-1}. This indicates that temperature plays a very important role in affecting the magnitude of the electrical conductivity of β-boron. According to equation (2), when the pressure remains constant, the conductivity should increase with increasing temperature, and the plot of $\ln \sigma$ versus $1/T$ should be a linear. Our result indicates that the transition behavior of β-boron is quite consistent with such a semiconductor behavior. Table 2 shows the activation energy obtained by a linear fit of the experimental data. It increases with increasing pressure. This expresses the effect of pressure on the energy barrier to charge transport. In addition, Schmechel *et al* proved that a series of six intrinsic traps levels exists, which are created by electron–phonon interactions in the crystal interior [25]. So it is speculated that the holes should be the dominant charge carriers in the above-mentioned range of temperature.

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Table 2. Activation energy for β-boron under 14.5 and 18.6 GPa by laser heating.

P (GPa)	E (eV)	δ_0 (s cm^{-1})
14.8	5.1×10^{-3}	1.7
18.6	8.3×10^{-3}	1.5×10^3

4. Conclusions

In conclusion, electrical conductivity measurements of β-boron were made via 'designer' diamond anvils. The plot of pressure against the logarithm of electrical conductivity is always linear in the pressure range we studied. This indicates that the conduction mechanism is invariable. Meanwhile, an irreversible conduction process with pressure is indicated. With temperature increasing from room temperature to 423 K, an inflexion of electrical conductivity at about 370 K appears, and this divides the curves into two different conduction processes. In addition, in an extended temperature range (1575–2224 K), semiconductor behavior is confirmed.

Acknowledgments

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