Metallization and Superconductivity of Molecular Crystal BI$_3$ under Pressure

Suzue Onoda and Katsuya Shimizu

KYOKUGEN, Center for Quantum Science and Technology under Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan
e-mail: onoda@djebel.mp.es.osaka-u.ac.jp

Abstract. Electrical resistivity measurement of boron triiodide (BI$_3$) have been performed at high pressures up to 70 GPa. At room temperature, the resistivity decreased rapidly with applying pressure. The temperature dependence of electrical resistance indicated metallization of BI$_3$ at 23 GPa. The superconducting transition was found above 27 GPa.

1. Introduction

A structural characteristic of molecular crystals is the difference in strength between the strong intramolecular bonding and the weak intermolecular bonding. Under pressure, this difference brings a variety of structural transitions, metallizations, superconducting transition, and molecular dissociations as a result.

In diatomic molecular crystal I$_2$, it was reported that the insulator-metal transition occurs at around 16 GPa [1], followed by the molecular dissociation at 21 GPa [2]. The superconducting transition of the monatomic iodine was observed at the pressure of about 22 GPa [3]. The pressure-induced metallization has been explained by the band overlap between the valence and the conduction band. In case of molecular crystal SnI$_4$, the metallization and superconducting transition occurs in the amorphous state under pressure [4,5]. It is expected that most of molecular crystals show metallization under pressure. However, the mechanism of metallization and dissociation is still unclear.

At ambient pressure and room temperature, BI$_3$ molecule, which is planar equilateral triangle form, crystallizes into hexagonal structure as illustrated in Figure 1 [6]. Our recent X-ray diffraction study revealed a structural phase transition at 6.9 GPa to new phase, and the molecular seemed to dissociate at the transition pressure [7]. At higher pressure, BI$_3$ crystal gradually became into opaque which may show the tendency of metallization of BI$_3$.

These molecules of I$_2$, SnI$_4$ and BI$_3$, the basic structure of which are formed by iodine, may show a similar metallization under pressure. Comparison of the phenomena under pressure of these similar molecular crystals would make a mechanism of metallization and molecular dissociation in molecular crystals clear.

Figure 1. A unit cell of crystalline BI$_3$. Molecules are layered to c-axis and form crystal.
To investigate the high pressure phenomena of BI$_3$, we performed the electrical resistance measurement at high pressure and low temperature.

2. Experimental
A compact diamond anvil-cell (DAC) was used to produce high pressure at low temperature experiments. We used nonmagnetic stainless steel 310S for a gasket material. Pressure was determined by a ruby fluorescence method at low temperature as well as at room temperature. Al$_2$O$_3$ powder was placed on the surface of gasket for electrical insulation. Since BI$_3$ is extremely hygroscopic, the sample was loaded into the center of the insulated gasket with small ruby chips. The electrical resistance was measured by 4-terminal method with Pt electrodes with typical measuring current of 500 nA. The pressure was applied at room temperature and we used a $^3$He/$^4$He dilution refrigerator in order to cool DAC down to low temperature of 60 mK.

3. Results and Discussion
The pressure dependence of the electrical resistivity $\rho$ of BI$_3$ measured at room temperature is plotted in Figure 2. At pressure range between 5 and 17 GPa, we observed rapid and continuous decrease of the resistivity. Above 17 GPa, the $\rho$ became almost independent to pressure which may indicate the metallization of BI$_3$. These results show that the metallization occurs at higher pressure than molecular dissociation in case of BI$_3$.

With applying pressure, the color of sample changes from transparent to opaque. Above 20 GPa, the sample became a little luster. To reveal the metallization of BI$_3$, we measured temperature dependence of the electrical resistance above 17 GPa.

The temperature dependence of the relative resistance $R/R_{20K}$ at several pressures in low temperature region is displayed in Figure 3. The negative temperature dependence was observed at 17 and 20 GPa; the characteristic behavior of semiconductor. This behavior was suppressed with applying pressure and disappeared at 23 GPa which shows that the metallization of BI$_3$ occurs at this pressure.
As applying pressure further, we found an abrupt drop in the resistance showing the superconducting transition below 1 K at 27 GPa as shown in Figure.3. The superconducting transition $T_c$ was determined as 0.5 K from the onset of the transition. We observed the positive pressure dependence of the $T_c$ as shown in Figure 4.

![Figure 4](image-url)

**Figure 4.** $T_c$ versus $P$ diagram for $\text{BI}_3$, $\text{I}_2$ and $\text{SnI}_4$. The arrow indicates the absence of superconductivity of $\text{BI}_3$ down to 35 mK.

Figure 5 shows the magnetic field dependence of the superconducting transition under constant pressure of 33 GPa. The transition temperature shifts lower temperature with applied magnetic field. The critical field $H_c$ is estimated 0.8 T with extrapolation.

![Figure 5](image-url)

**Figure 5.** The temperature dependence of the relative electric resistance of $\text{BI}_3$ at low temperature under various magnetic field at $P = 33$ GPa.
4. Summary
We performed the electrical resistance measurements of Bi$_3$ under high pressure and low temperature. At room temperature, the resistivity decreases rapidly. By the temperature dependence of the resistance, we determined the metallization pressure of Bi$_3$ is 23 GPa. We also found the superconducting transition at 27 GPa. The positive pressure dependence of the $T_c$ was observed at pressure between 27 and 65 GPa with $T_c$ changing from 0.5 to 1.9 K.

According to the results by X-ray diffraction study, we conclude that the metallization occurs at higher pressure than molecular dissociation in case of Bi$_3$. This differs from the behavior of I$_2$ and SnI$_4$. However, the superconductivity of all three molecular crystals appears for pressures near 25 GPa.

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