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Superconductivity from insulating elements under high pressure

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ABSTRACT

The insulating and superconducting states would seem to have very different characteristics. Can any insulator become a superconductor? One proven method, doping an insulating material with carriers, can create itinerant states inside the gap between the conduction and valence bands. Another method is to squeeze the structure by applying pressure. Pressure can expand the bandwidth and also narrow the energy band gap. So the first step to turn an insulator into a superconductor is to make it metallic. Here we review our experimental research and results on superconductivity induced by applying pressure to insulating molecular systems such as elemental molecules.

Contents

1. Introduction

Molecular solid is typical insulator. For example, hydrogen forms a diatomic molecular crystal with covalent bond. The electron was occupied to form the covalent bond and then does not work for the conduction between each atom. When the molecular solid is compressed, the inter-molecular distance decrease and each molecule get closer. The intra-molecular distance also decrease but the pressure influence is smaller than inter-molecular distance, which determined by weak van der Waals force. At the pressure where two distances (inter and intra distance) become same, the determination of molecular no longer exists. This is "pressure-induced dissociation" and the metallization by released free electrons is expected. Hydrogen forms a diatomic molecule of H_2, is expected to be a metal which shows the room-temperature superconductor [1]. This has motivated us to squeeze hydrogen over long periods; however, no experimental report of the solid metallic hydrogen exists up to now. Here our experimental results are reviewed with halogens and chalcogens as alternatives to hydrogen in this paper.

2. Halogen; iodine, bromine

Metallization of iodine under high pressure was firstly reported by Drickamer and Balchan [2] and confirmed by Sakai et al. [3] with results on temperature dependence of the resistance. They claimed the existence of the metallic molecular phase followed by the monatomic structural phase, and the monatomic iodine metal showed the general temperature dependency of Bloch-Gruneizen equation. The superconductivity of iodine was firstly found in the monatomic structural phase (II) by our resistance measurements under high pressure using a diamond-anvil cell (DAC) [4].

The superconducting transition temperature, T_c was low as 1.2 K at 22 GPa as shown in Fig. 1. The superconductivity seemed to appear after the molecular dissociation (in the monatomic phase), however recent careful and more hydrostatic experiments showed the molecular metallic phase also showed the superconductivity [7]. Iodine shows structural phase transition [8] and the T_c and the pressure dependence vary according to the structure [9].

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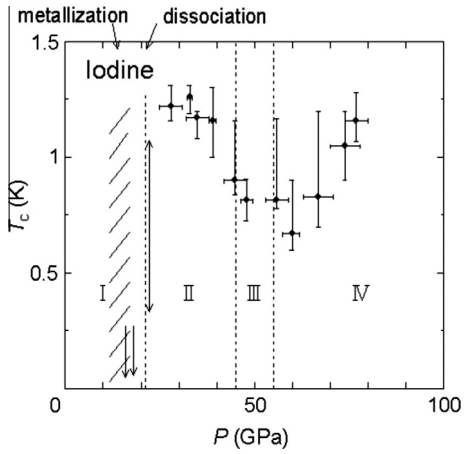

Fig. 1. Pressure dependence of T_c of iodine [4]. The horizontal and vertical error bars indicate the pressure distribution and width of the transition temperature, respectively. Dotted lines show the pressure boundaries between phase-I, II, III and IV given by the extrapolations from the ones obtained at room temperature. Please note that phase-V [5] was not found at the moment.

The Hall effect measurement at high pressure [6] (Fig. 2) revealed that the carrier is not electron but hole, and the density increase very rapidly to the pressure of the molecular dissociation showing insulator–metal transition.

The abrupt increase of the carrier density, towards molecular dissociation may be closely related with the appearance of superconductivity of iodine. The lighter halogen elements such as bromine (Br_2), chlorine (Cl_2), fluorine (F_2), and even hydrogen (H_2) should follow the iodine case analogously, however, only bromine was found to be metallize and superconduct at around 80 GPa giving T_c of 1.5 K [10]. Fujihisa et al. [11] claimed the scaling law on the pressure dependence of the reduced lattice constant and the metallization for halogen elements. According to their estimation, the metallization pressure of chlorine and fluorine is considerably high, however T_c is not observed experimentally yet.

3. Chalcogen; sulfur, oxygen

Pressure-induced successive structural and insulator–metal transition was observed in VIb group elements of selenium (Se) and tellurium (Te). The metallization pressure is found to increase towards lighter element and the superconductivity is also observed [12–14] in the case of them with T_c of 4 K and 5 K, respectively.

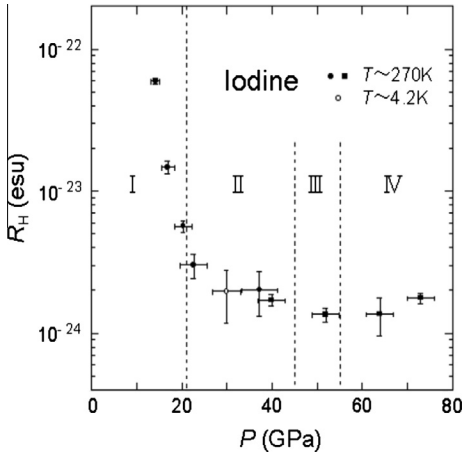

Fig. 2. The Hall coefficient as a function of pressure of iodine [6]. Broken lines indicate the structural phase boundary. Please note that phase-V [5] was not found at the moment.

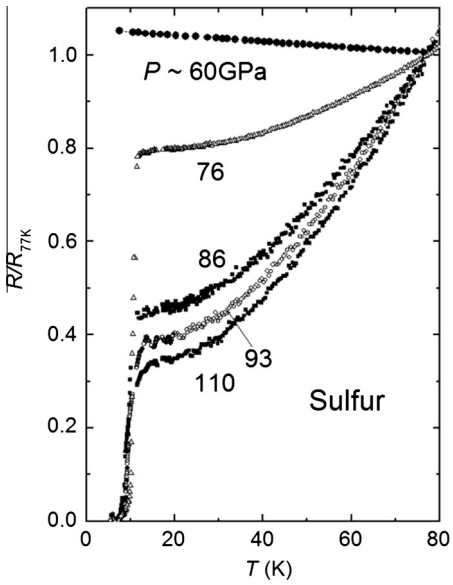

Fig. 3. Electrical resistance drop of sulfur at pressure above 60 GPa. The electrical transition from semiconductor (60 GPa) to superconducting metal ($P > 76$ GPa) was clearly observed.

Higher T_c for metallized sulfur and oxygen under higher pressure than Se and Te is expected. Luo et al. [15] reported the optical evidence of the metallization of sulfur at pressure between 88 and 95 GPa. The metallization of sulfur was claimed by electrical resistance measurement by Bundy and Dunn [13] with strong reduction of the resistance at room temperature, and a possible superconductivity was reported by Stepanov and Yakovlev [16].

We clearly confirmed that sulfur undergoes metallization and superconductivity at around 70 GPa using our DAC technique with the maximum T_c of 15 K at around 100 GPa [17] as shown in Fig. 3. The T_c increases with pressure and Struzhkin et al. [18] investigated the higher pressure dependence of T_c by ac susceptibility measurement and found the T_c jumps from 14 K to 17 K at around 160 GPa where structural transition from bcc to beta-Po phase. At the moment T_c of sulfur was the highest in chalcogen element.

Thus we could expect the higher T_c for oxygen than sulfur. The optical observation by Desgreniers et al. [19] claimed the metallization accompanied by the band overlap at 98 GPa, and the structural transition associated with the metallization was reported by Akahama et al. [20] Analogous to the case of iodine, the molecular dissociation seems to need for the superconductivity, however these results showed that the molecular state still remains at the metallic phase. We tried performing direct observation of the metallization by measuring electrical conductivity. Fig. 4 shows the electrical resistance of oxygen under pressure with an exponential decrease of the resistance from 60 to 100 GPa with indicates the appearance of conductive oxygen around 100 GPa. Shiny reflection light from the surface of oxygen through a microscope was simultaneously observed. The slope of temperature dependence of resistance could judge metallization as shown in Fig. 5.

The change of the slope was found around 100 GPa which indicates the electrical transition from semiconductor to metal. The resistance drop at 0.6 K was observed at 98 GPa which attributed to the transition to superconductivity [21]. The superconductivity was definitely confirmed by detection of Meissner effect and the magnetic field dependence of the resistance drop as shown in Figs. 6 and 7. The observed T_c of oxygen at around 1 K was unexpectedly low compared to the results in other VIb group elements. Considering that the superconductivity was observed in monatomic metallic phase in other VIb elements, higher T_c in oxygen