Review Article

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High-Pressure Research on Superconductivity at SPring-8

Although superconductivity is known as a very rare phenomenon that occurs in a limited number of compounds, many superconductors have been found and synthesized under high-pressure conditions. Actually, almost half the elements in the periodic table become superconductors under ambient and high-pressure conditions.

Pressure changes the distance between atoms and can also change the structure. Thus, the properties of a material, such as superconductivity, can be controlled via the pressure. To study and uncover the potential of materials, the use of a high pressure can be a very effective and powerful methods. Here we review our high-pressure research on superconductors and related materials at SPring-8.

1. Beamline improvement for multipurpose measurements: XRD, electrical resistivity, and Raman scattering under a high pressure and low temperature

A newly developed system for simultaneous X-ray diffraction (XRD) and Raman scattering spectroscopy measurements was installed in the upstream experimental hutch of BL10XU. The crystal structure at high pressures is one of the most important points in the study of the high-pressure phenomena of materials, such as pressure-induced insulator-to-metal transition, superconductivity, and so on. However, when data for the crystal structure and electrical resistance have been obtained in separate experiments and compared, discrepancies have been found between them in not only the pressure but also the pressure condition such as the pressure hydrostaticity. To solve this problem, resistance measurements at a high pressure and low temperature were performed on the diffraction measurement stage in the experimental hutch of BL10XU.

1-1. New simultaneous measurement system in BL10XU

Figure 1 shows the system in the experimental hutch of BL10XU. The X-ray diffractometer consists of a flat imaging plate detector (IP) and a horizontally rotating ω -goniometer on a heavy-duty y-z stage. High-pressure and low-temperature experiments are performed using a helium-gas-flow-type 4 K cryostat combined with a helium-gas-driven membrane diamond anvil cell (DAC). To minimize the vibration of the sample in the DAC caused by



Fig. 1. Photograph of the cryostat equipped with Raman scattering and resistance measurements equipment used in high-pressure studies.

the cold head due to the motion of the refrigerator, a bundle of flexible copper wires is used as the heat link between the cold stage and the DAC.

The cryostat has two transparent windows: one is for the synchrotron X-ray beam input (upstream) and the other is for diffraction measurements (downstream). The micro-Raman scattering spectroscopy system was installed in the up-stream. The objective lens of the Raman microscope has a long working distance, and the laser beam and Raman signal are introduced onaxis to the input X-ray beam by using a glassy carbon mirror that is transparent to X-rays.

The optics of the Raman spectroscopy system and pressure control system were installed outside of the experimental hutch and they are connected by optical fibers and stainless-steal high-pressure gas tubes, respectively. This allows us to simultaneously obtain XRD and Raman scattering spectra from samples under precise pressure control.

1-2. Electrical measurement setup in high-pressure device (DAC)

A pair of ~1/3 carat diamond anvils with an 8-degree beveled design, a top surface diameter of 50 or 100 µm, and a culet of 300 µm is routinely used. When performing an electrical resistance measurement at high pressure, the insulation of the metal gasket is essential. Figure 2 shows the typical arrangement of the gasket and electrodes we use (in this figure, the sample was lithium). The rhenium gasket is preindented to ~30 µm thickness and a thin part of the indent is removed. An insulating material powder (such as diamond, c-BN, or Al₂O₃) is placed in the gasket and a sample hole of 30-50 um diameter is made at the center of the gasket. The electrodes deposited on the upper diamond consist of a bottom layer of titanium (Ti) and a top layer of copper (Cu). The deposited electrodes with the sample and with platinum (Pt) foil electrodes on the insulating layer. The electrical resistance is measured by the conventional four-terminal method with an AC current.



Fig. 2. Schematic of the sample (Li) and the electrode in the DAC.

2. Examples of results

In this section, recent works on superconductivity and structural studies carried out at BL10XU are reviewed.

2-1. Pressure-induced superconductivity, metal-to-insulator transition, and re-entrant metal phase of *lithium*

We previously reported that the superconducting transition temperature of lithium is enhanced by pressure from a low temperature of 0.4 mK under ambient condition to 20 K [1]. A theoretical calculation predicted the possible formation of an insulating or semiconducting state of lithium at ~100 GPa [2]. Here we report the dramatic changes in the electrical and structural properties of lithium upon applying pressure.

An anomalous increase in the electrical resistivity at 25 K was observed with increasing pressure as shown in Fig. 3, where the vertical broken lines indicate the structural phase boundaries at the same temperature determined by *in situ* XRD studies. When the pressure reached ~70 GPa, the electrical resistivity abruptly increased by about five orders of magnitude and saturated at ~94 GPa.

It was found that the huge increase in the electrical resistivity is accompanied by a structural transition from cI16 to higher-pressure phases named hp-I (Li-VI) and hp-II (Li-VII) [3].

At further compression up to 137 GPa, the electrical resistivity decreased by about four orders of magnitude at a pressure of 100–120 GPa, indicating closure of the band gap as shown in Fig. 4. At the same time (at 120 GPa), a structural transition from Li-VII to a new phase (Li-VIII) was observed. The temperature dependence of the resistivity changed from negative to positive, indicating a transition from a semiconductor to metal. In addition, a drop in the resistance (which may indicate superconductivity) was also observed at ~10 K [4].

This study demonstrated the existence of a semiconductor phase between two distinct metallic phases as shown in Fig. 4. The compressed light alkali metal Li has contributed to broadening our understanding of metals.

2-2. Incommensurate structural phase in molecular *iodine*

Solid iodine is a typical diatomic molecular crystal, for which it has been reported that metallization occurs at 16 GPa and molecular dissociation occurs at 21 GPa [5,6]. Iodine changes its structure from a diatomic molecular crystal to a single atomic metal



Fig. 3. Resistivity of lithium at high pressure measured with XRD.

under pressure. However, in a recent hydrostatic pressure experiment that used helium as a pressure medium, a new structural phase (phase-V) was observed at a pressure around 24-28 GPa [7]. Phase-V takes an incommensurate structure before dissociation from the molecule to the atomic metal. We consider that this intermediate phase of iodine may be one of the keys to clarifying the pressureinduced phenomena of molecular crystals. Here we report electrical resistance measurements of phase-V as a function of temperature down to 6 K while simultaneously performing XRD measurements. A gas-membrane-type diamond anvil cell (MDAC) made of nonmagnetic CuBe alloy was used. The iodine sample was treated in water- and oxygen-free argon gas in a glove box and placed into the gasket without a pressure-transmitting medium. Pressure was determined by the ruby fluorescence method at a low temperature as well as at room temperature. The electrical resistance was measured by an ac fourterminal method with evaporated Pt electrodes at a typical current of 500 nA. The pressure was applied at room temperature. The iodine transformed completely into phase-V at 24 GPa even without a pressure-transmitting medium. Vibration of the refrigerator used in the experiment was suppressed to less than 10 micron. A synchrotron X-ray beam was accurately focused onto the sample at the 20-micron gap between two electrical probes and the diffraction was collected by an imaging plate detector. During the cooling of the MDAC, the pressure, electrical resistance, and diffraction spectra were monitored at

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Fig. 4. Temperature-pressure phase diagram of lithium. SC: superconducting phase. The vertical lines indicate the structural phase boundary at 25 K.

same time and are shown in Fig. 5. The resistance decreased with decreasing temperature down to 6 K, suggesting that phase-V is metallic. The search for superconductivity at a lower temperature in phase-V is ongoing.



Fig. 5. (a) XRD spectra of iodine in phase-V at different temperatures and (b) temperature dependence of the electrical resistance at a fixed pressure of 24 GPa.

2-3. *Calcium*, the highest temperature superconducting element, and its structure

We have reported the highest temperature superconductivity for an element, which calcium (Ca) was with a transition temperature of 29 K at 216 GPa. At ambient pressure and temperature, Ca forms an *fcc* structure (Ca-I). With increasing pressure, successive phase transitions to Ca-VII were experimentally observed as shown in Fig. 6(a). The high-pressure phase Ca-VII has been suggested to be the host-guest structure already reported for the highest temperature superconducting phase of Ba [8,9]. We performed powder XRD and electrical resistance measurements of Ca under high pressure in order to search for the highpressure phase of Ca-VII with the hostguest structure and superconductivity.

A Ca sample was set in a DAC for XRD measurements and pressurized up to 241 GPa at room temperature. High-quality powder patterns of Ca in the high-pressure region above 200 GPa were obtained. The structure of Ca-VII was determined by this XRD experiment combined with a density functional theory calculation and was found to be an unusual host-guest-type structure [10].

Figure7 shows the superconducting transition temperatures of elements in the periodic table as heights, including Ca with the highest temperature. The height is proportional to the highest (maximum) superconducting temperature ever observed for each element. Most of the maxima were recorded at ambient pressure, but the remainder were observed at higher pressures. In addition, for some of the elements, superconducting transition temperature $T_{\rm c}$ continues to increase with the pressure. According to this figure, the high- T_c elements are located at near the horizontal edges of the table. One of the ultimate goals of superconductivity research is the experimental realization of metallic hydrogen as a room-temperature superconductor. This is expected to occur above a pressure of 450 GPa, which has never been achieved for hydrogen.

We reported our recent research towards achieving metallic hydrogen in the next two subsections.

2-4. Transition to *metallic fluid hydrogen* at high temperature and high pressure

Hydrogen is expected to metallize and show high-temperature superconductivity at a very high pressure of ~500 GPa. On the other hand, hydrogen under high temperature and high pressure (HTHP) condition is also expected to be metallic in the fluid phase, which is realized in giant planets such as Jupiter and Saturn. In previous shock-pressure experiments, the metallic behavior of fluid hydrogen was observed [11]. However, the transition boundary and the properties of metallic fluid hydrogen have not yet been clarified. Thus, we generated a static HTHP condition and examined the region of stability of hydrogen using a laser heated diamond anvil cell (LHDAC).

We heated hydrogen under a high pressure with an infrared laser and examined the heating efficiency by considering the relationship between the temperature and the laser power. XRD and Raman spectroscopy measurements were performed before and after the laserheating experiments and they showed that no chemical reaction occurred between hydrogen and surrounding materials. The results show anomalies in the heating efficiency, which are likely to be due to the phase transition of hydrogen from a diatomic fluid to a monoatomic fluid in the pressure range 82-106 GPa as shown in Fig. 8. These results are in good agreement with the previously proposed plasma phase transition boundary [12]. This technique is expected to help us experimentally to realize the solid metallic phase of hydrogen.



Fig. 6. (a) Structural transitions and (b) superconducting temperature of Ca at high pressure.



Fig. 7. 3D periodic table of elements, where the heights represent superconducting temperatures.

2-5. Structure of *sulfur hydrides* with superconductivity above 200 K

Superconductivity above 200 K was recently reported in highly compressed hydrogen sulfide (H₂S) [13]. It has been proposed that this material decomposes into elemental sulfur and a hydride with a higher hydrogen content, which is responsible for the high-temperature superconductivity [14]. We measured the crystal structures of the superconducting phases of hydrogen sulfide and deuteride sulfide in their normal (at room temperature) and superconducting states by XRD measurements combined with electrical resistance measurements.

 H_3S and D_3S were compressed to 150 GPa in a DAC by a previously reported process [12] and cooled to 10 K in a cryostat. The resistivity was



Fig. 8. Phase diagram of hydrogen. The gray area is the theoretically proposed transition line.

monitored throughout the cooling process. The critical temperature and zero resistivity were observed at around 180 K. The collected XRD data showed good agreement with the theoretically predicted sulfur atom position in the structures of the R3m and $Im\overline{3}m$ phases and pure sulfur (β -Po structure). The position of the hydrogen atoms cannot be determined from the XRD measurements as the hydrogen atom is a weak scatterer. No difference was observed between the spectra obtained at 10 K and room temperature, and from the pressure dependence of the transition, we can conclude that the highest critical temperature of 200 K corresponds to the $Im\overline{3}m$ phase as shown in Fig. 9 [15].

3. Summary

The benefit of simultaneous measurements in high-pressure experiments, especially in the highpressure region, is worth noting. This is because when some physical properties are measured in separate experiments, it is not guaranteed that the samples are under exactly the same pressure, stress, and temperature conditions. In order to demonstrate the relationship between the crystal structure and electrical characteristics, simultaneous XRD and electrical resistance measurements of the same sample are the most straightforward solution.



Fig. 9. Pressure dependence of the superconducting transition temperature T_c of H₃S (black) and D₃S (red).

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