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# HIGH PRESSURE APPARATUS FOR *IN SITU* X-RAY DIFFRACTION AND ELECTRICAL RESISTANCE MEASUREMENT AT LOW TEMPERATURE

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A new high pressure apparatus with cubic anvil device has been developed to carry out X-ray diffraction and electrical resistance measurement simultaneously up to 10 Gpa at low temperature down to 5 K. This apparatus consists mainly of a uniaxial press for pressure generation, an X-ray diffraction system with energy dispersive solid state detector and a cryostat. We show the typical results obtained by this apparatus.

## 1. Introduction

High pressure is very effective tool for research of discovering new phenomena and of exploring new materials. For example, some materials undergo superconducting transition under high pressure. Also, it is well known that some insulators become metallic at high pressure. Conversely, there are some singular materials in which metallic state becomes unstable for insulating state at high pressure. Changes in these physical properties are induced by the changes in the atomic positions originated from the changes in the volume at high pressure.

Recently, much attention has been drawn to pressure effects on physical properties of materials. Such as the study of pressure induced phase transition, the pressure effect on the superconducting transition temperature of high-T<sub>c</sub> oxide superconductors, the change in electronic properties of the heavy fermion system at high pressure, and the peculiar phenomena of organic conductors under high pressure are interesting topics. Thus, it has been required for the apparatus to realize the highly reliable measurements of physical properties at low temperatures under high pressure. Especially, to clarify the origin of such changes in the physical properties, structural refinement at low temperatures under high pressure is an important research project.

In order to examine the physical properties at high pressure, it is, of course, desirable to apply the pressure as high as possible to the sample. However, one cannot simply assert the higher, the better. This

remark may sound strange, but this means in a case using the pressure as the tool for elucidating the physical properties that the physical quantities should be investigated in such pressure regions where no structural change occurs. That is, the pressure is effective for tuning the electronic structure. Besides, the pressure uniformity is important for the experiments.

Among conventional high pressure apparatus, the piston-cylinder system is excellent in terms of hydrostatic conditions although its maximal pressure is no more than 3 GPa or so. This type is easy to handle and is widely used for studies of the physical properties at low temperatures. With this type, however, it is difficult to conduct crystallographic study like X-ray diffractometry. On the other hand, the diamond anvil cell being optically transparent can generate pressures beyond 100 GPa and therefore its application is extended to structure analysis, infrared spectroscopy, Brillouin scattering, etc. But this type is inferior in the uniformity of pressure and, moreover, the quantity of sample it can accommodate is very small. Because of such limitations, the diamond anvil cell is not suitable for quantitative evaluation of other physical quantities, such as electric and magnetic properties.

High pressure apparatus of cubic anvil type has so far been used for various researches under pressure up to around 10 Gpa, for example, structural studies above room temperatures obtained by X-ray diffraction and studies of the pressure effect on the physical properties at low temperature obtained by the

electric measurements such as electrical resistance. But as compared with the measurement of electrical resistance, it is far more difficult to carry out X-ray diffraction experiments with the cubic anvil type apparatus at low temperature under high pressure. Hence no reports have been published yet on such work. In the structural study at low temperature under high pressure, the high quality results will be obtained by using neutron diffraction in the pressure region below about 1 GPa [1]. But there are no established measurement techniques yet to deal with higher pressure regions than 1 GPa. For studies of the pressure effects, especially in the case that changes in physical property are observed at low temperatures, it is essential to examine whether or not a structural change occurs. From this point of view, we worked on the development of a high pressure apparatus with cubic anvil press which should permit X-ray diffraction experiments and electrical resistance measurement simultaneously at low temperature.

With the cubic anvil press, the amount of sample can be 3 to 5 orders of magnitude greater in volume than with the diamond anvil cell. This merit enables measurement of the physical properties with a precision comparable to that under ambient conditions. Thus far its major application has been X-ray diffraction experiments at high temperature under high pressure with a built-in heater by taking advantage of the large capacity for sample. This time, we attempted to stuff an X-ray diffraction sample into the upper gasket part, as will be explained later, while installing a sample for electrical resistance measurement into the lower part. In this way we challenged simultaneous measurements of X-ray diffraction and electrical resistance at low temperature under high pressure.

## 2. System Configuration and Characteristics

Our cubic anvil type cryogenic high pressure generation system is based, as the prototype, on the low temperature and high pressure apparatus [2] being operated at the Institute for Solid State Physics, the University of Tokyo. Some new design attempts are incorporated specifically for low temperature X-ray diffraction experiments. This apparatus is made up of a uniaxial type 250-ton press supported by two columns, an X-ray diffraction system, and an adiabatic type vacuum cryostat which accommodates a cubic anvil for high pressure generation (Fig. 1). The cubic anvil section was initially designed for measurement of electrical properties in a temperature



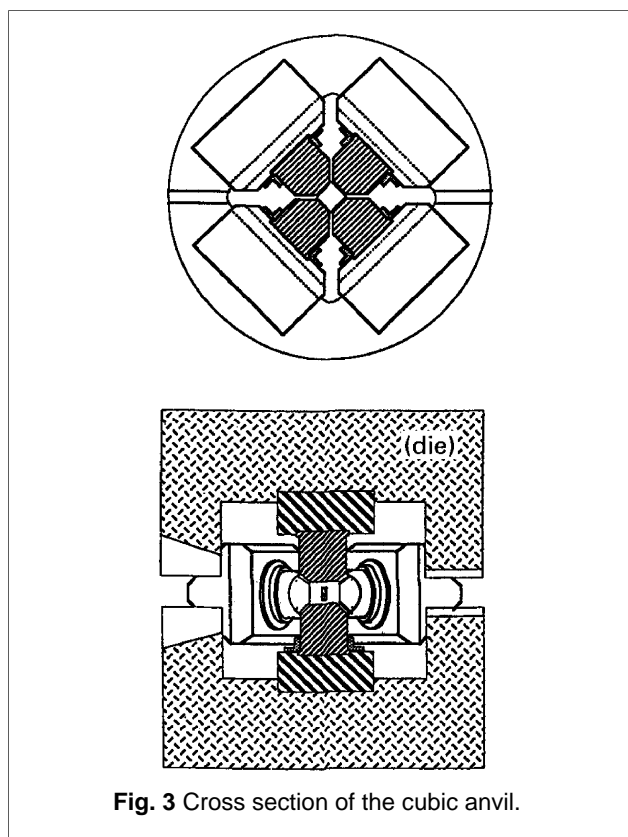
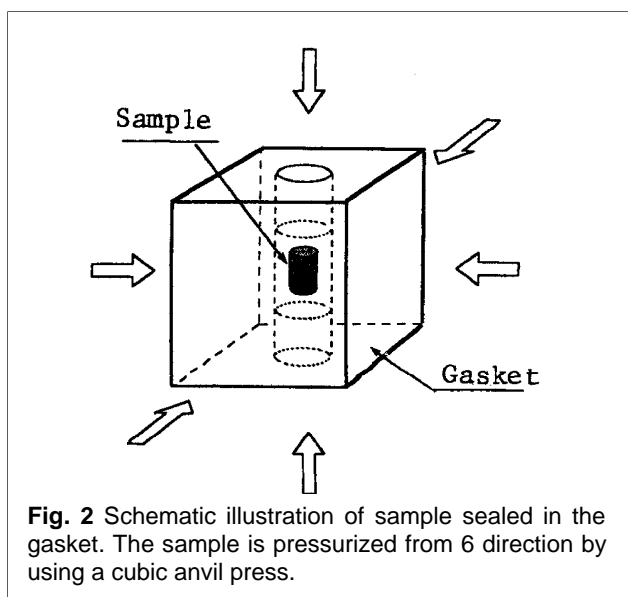
Fig. 1 Photograph of apparatus

range from room temperature to low temperature (liquid helium temperature) under high pressures of 10 GPa in maximum and of 9 GPa for routine operation. At the same time it was aimed at measurement of lattice constant with the same precision as at room temperature and atmospheric pressure.

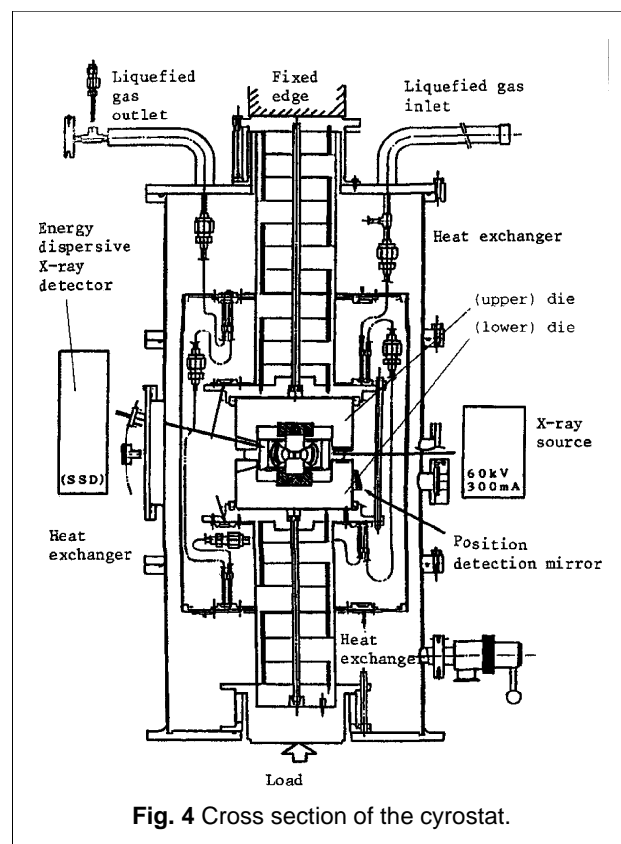
With a newly developed optical control system, the apparatus has made it possible to conduct X-ray diffractometry in low temperature/ high pressure regions, so far regarded as difficult techniques. Further, a newly prepared low temperature controlling device has made it possible to upgrade physical property studies that excel in quality and reliability compared with earlier studies using conventional systems. The characteristics of each component will be discussed in the following sections.

### 2. 1. Pressure Generation

The cubic anvil device is so designed that a gasket as a pressure medium is compressed evenly from six directions with six anvil tops, thereby producing a hydrostatic high pressure for a sample sealed in the gasket (Fig. 2). Two of the six anvil tops are directly fixed to retaining dies arranged at upper and lower part of a sample section, respectively. In operation these upper and lower anvils are moved closer to each other by a certain distance, and this displacement will cause the other horizontally arranged four anvils to slide on a 45° slope in the retaining dies, respectively, by the same distance toward the center. This means that a uni-axial press



drives all anvils evenly at the same time (Fig. 3). The anvil top is made of tungsten carbide and the retaining die is Ni-Cr-Mo steel. A slit is worked in each die by taking into account an X-ray diffraction experiment under high pressure at low temperature. The gasket material is a mixture of amorphous boron and epoxy resin in 4:1 weight ratio, both of which are characterized by less X-ray absorption.



To serve as the pressure system it is necessary to transmit loads adiabatically to the anvil tops at low temperature. To this purpose, the thick plates made of fiber reinforced plastics (FRP) are used, as shown in Fig. 4 of a cross-sectional construction. As shown in this figure, the cubic anvil device is placed between both ends of pressure transmitting FRP column. In the operational condition, because there exists the temperature gradient from room temperature outside of cryostat to the liquid helium temperature at the sample position, the sample pressure will vary due to the change in the load caused by the thermal expansion/contraction of FRP column with increasing/decreasing temperature. As a counter-measure, the oil pressure system driving the uniaxial press is so designed that a change in load is automatically corrected and that a constant pressure is always applied to the sample section despite temperature changes.

## 2.2. Cryostat

By using the cubic anvil device, we planned to do experiments for physical properties over a temperature range from low to room temperatures at high pressure, such as the lattice constants, the electrical resistance and the change in magnetization. For these experiments, a cryostat is required to control the

temperature of the cubic anvil device consisting of the retaining dies and the six anvils, and the gasket at the center of which a sample is sealed.

To cool down such large device to the liquid helium temperature, the following construction is generally required. That is, an adiabatic container for liquid nitrogen should be arranged as the outermost component. Then another adiabatic container for liquid helium should be placed inside. Further, a cubic anvil device for high pressure generation should be accommodated in the latter adiabatic container. Now, if measurement concerns only the physical properties like the electric and magnetic properties, it is possible to conduct it in a virtually equilibrium state without considering special temperature control. This is because the heat capacity of what is contained inside is so large that temperature changes are relatively slow enough compared with the duration of time required for each measurement at the respective temperatures. Whereas, if an X-ray experiment should be carried out concurrently, there may occur a need to hold at each measuring temperature for several hours or more in order to get a diffraction pattern with a good signal-to-noise ratio. For the temperature control, therefore, a desirable construction is that adiabatic space should be set up in a liquid helium environment so that the high pressure generator may be installed in that space. This is not easy in practice because of restrictions coming from costs and the overall dimensions. To resolve this problem, we decided to employ a thermal conduction system designed to cool the cubic anvil device indirectly by the flow of refrigerants, such as liquid nitrogen and liquid helium. That is, there is no storage for liquid gases inside the cryostat. Instead, a heat exchanger is mounted to each retaining die, and operated by the flow of liquid nitrogen for temperatures down to 80 K and subsequently liquid helium for temperatures lower than that. As a result, just a single stainless steel sheet can serve as the outer wall of the cryostat to hold the inner vacuum. Thus, despite the provision of a radiation shield, a space around the dies is enough to prepare the sample for experiment. Besides, although we were initially concerned about if we could attain 10 K or so, the temperature proved to be 5 K in a preliminary experiment without load and turned out to be below 7 K in an actual experiment. We intend to aim at an even lower temperature sometime in future. To realize it, however, we must expect some trial-and-error process.

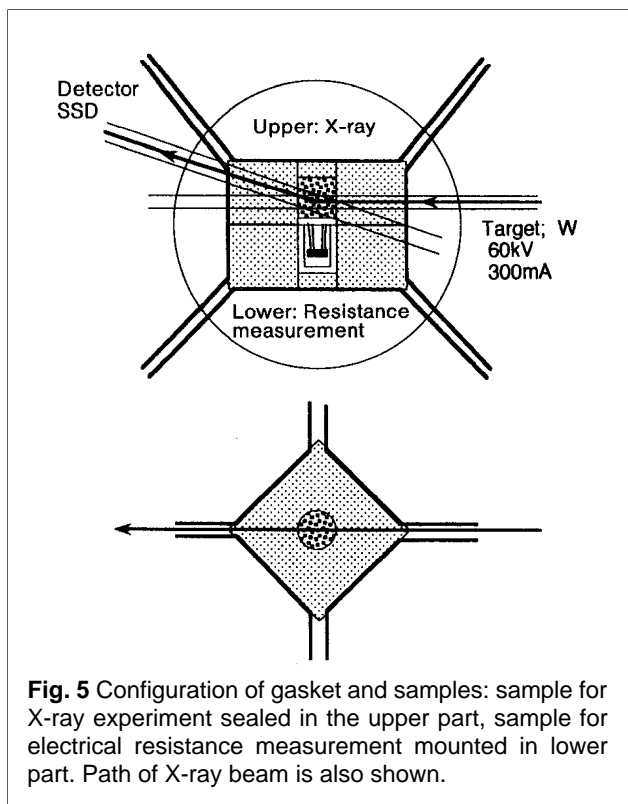
As mentioned previously, the load is transmitted to the anvil tops from the press head via the FRP column. Under the operation in this configuration, to protect the cryostat from unexpected stresses, the FRP column is mechanically separated from the cryostat by means of bellows. Our design is also such that by using this bellows, the position of the cryostat can be controlled independently against the position of sample section which moves due to the pressure and temperature changes.

### **2.3. In situ X-ray System**

In X-ray experiment at high pressure, it is not allowable to use much quantities of sample for the condition keeping the homogeneity of the applied pressure. It is, therefore, less than approx. 2 cubic millimeters. In addition, the gasket (pressure medium), etc surround the sample. Due to such restrictive conditions, the intensity of the resulting diffraction pattern is fairly lower than that obtainable by ordinary X-ray diffraction experiments. This is why an X-ray diffraction experiment under high pressure is difficult; hence it will be desirable to prepare a powerful X-ray source. For the X-ray source, we use a separate type (tabletop) tungsten rotating anode (the maximum output: 60 kV-300 mA) assembly made by Rigaku Corporation, and the energy dispersive method is applied for the X-ray detection by using a solid state detector (SSD).

The X-ray optical system is composed of the aforementioned separate type X-ray source, an incident collimator, a receiving collimator, and an SSD mounted on the goniometer. An installing stage for X-ray source is mounted on an X-ray goniometer table, and equipped with adjusting mechanisms for three directions. That is, X-Y-Z directions (X. parallel to the X-ray beam, Y. horizontal and perpendicular to X, Z. vertical), The X-ray goniometer table with the X-Y-Z stage is installed to the main body of the press frame. This makes it easy to adjust the X-ray optical axis. For the Z-direction adjustment of the goniometer table, an inverter is used allowing remote-control operation and automatic control (to be mentioned later). The incident and scattered X-ray collimators are installed to the cryostat via the bellows, but they are mechanically isolated from the cryostat to also allow fine adjustment for the optical alignment.

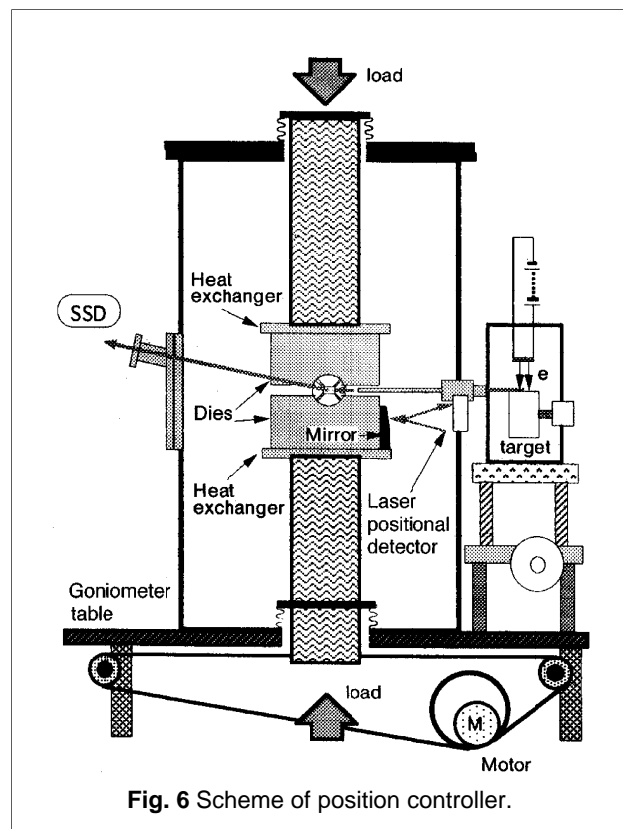
In this X-ray diffraction experiment, the incident X-ray beam passes through a narrow gap between the flanks of the anvil tops and impinges on a sample



**Fig. 5** Configuration of gasket and samples: sample for X-ray experiment sealed in the upper part, sample for electrical resistance measurement mounted in lower part. Path of X-ray beam is also shown.

stuffed in the gasket (also serving as a pressure medium). The resultant scattered X-rays are counted by the GE-SSD (Fig. 5). For the liquid nitrogen container to cool the Ge detector, a 7.5 liters large capacity one is employed with consideration given to the possibility of a long experiment time over several days.

Now, as the pressure rises, the anvil gap becomes gradually narrower. In addition, as shown in Fig. 4, the press head (ram) is arranged at the bottom of press frame, and the top of FRP column is fixed to the top bolster of press frame. For the reason, when the load is applied from the bottom, the position of the sample section will also gradually rise due to a reduction in the gap and the compression of the FRP. Consequently, there occurs a deviation in the relative position of the Z-direction between the X-ray beam and sample making it difficult to obtain an X-ray diffraction pattern. To cope with this, a positional detector is installed to the cryostat and it monitors a change in the sample position. Upon receiving its output, the goniometer table is driven by the inverter motor. In this way, an adjustment can be made at all times to keep constant the relative position between the X-ray beam and sample (Fig. 6).

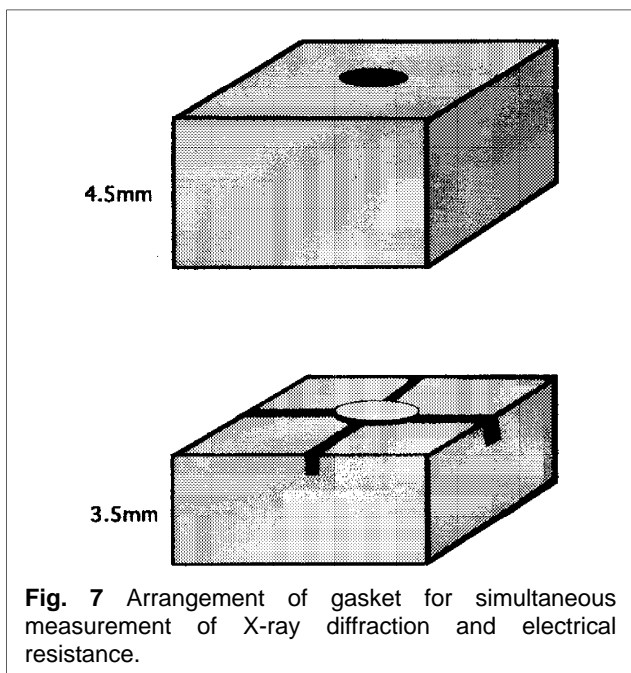


**Fig. 6** Scheme of position controller.

#### 2.4. Simultaneous Measurement of Electrical Resistance with in situ X-ray Diffraction

A 4-terminal method is employed for electrical resistance measurement. For measurement of the pressure effect on electrical resistance, we conducted it in similar way [2,3], which had already been executed at the Institute for Solid State Physics, the University of Tokyo. Further, when an X-ray diffraction experiment should be made concurrently, the configuration of a sample section is slightly modified. The following is our present method, which we have attained after repeating trial and error.

Because a set of anvil tops with 6 mm on edge of square face is available for enough sample space, we used it for simultaneous measurement of X-ray diffraction and electrical resistance. As a gasket, the cube of boron-epoxy is used; each edge of which is 8 mm long. In practice, the gasket was divided into two pieces, upper part with 4.5 mm high (4.5x8x8 mm) and lower part with 3.5 mm high (3.5x8x8 mm). A 2 mm dia. hole was made in the upper part to use as a sample chamber for X-ray measurement. Likewise, a 3 mm dia. hole was made in the lower part and a Teflon inner cell for electrical resistance measurement was inserted into the hole. Figure 7

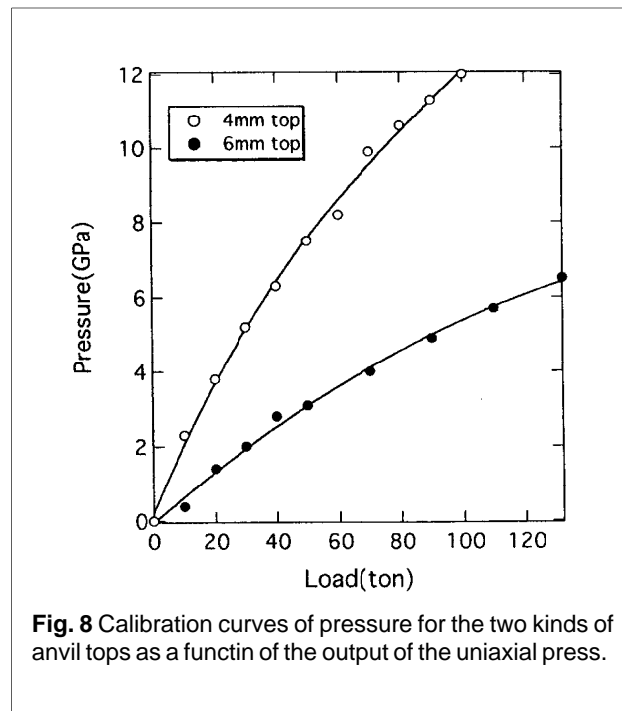


shows the gasket as a pressure medium and the sample configuration.

For electrical resistance measurement, Au wire of 20 microns diameter is used as lead wire for a sample. It is attached to the sample surface with gold paint contact. Then the lead wire attached sample is inserted into the Teflon cell filled with Fluorinert liquid as a pressure medium. At the outside of the cell, the lead wire is connected with gold foil (50 micron thickness X500 microns width) before coming out to the square face of anvil top. The lead wire, four in total, is electrically connected to each of the four anvil tops arranged horizontally. On this occasion, the four anvils are electrically insulated from the retaining dies by means of Teflon sheet and FRP sheets. At the time of actual measurement, in order to make correction for the origin of a digital voltmeter and for the thermoelectromotive force at the sample, polarity inversion was made about the electric-current.

### 3. Measurement of Pressure and Temperature

The pressure generated on this apparatus was calibrated by the change in the lattice constant of NaCl, the equation of state of which is well known. So far it has been confirmed at room temperature that the anvil tops with a 4mm edge of square face and a 6 mm one can respectively generate 12 GPa (9 GPa for a regular use; the anvil top was damaged at 12 GPa) and 6 GPa. Figure 8 shows a pressure calibration curve.



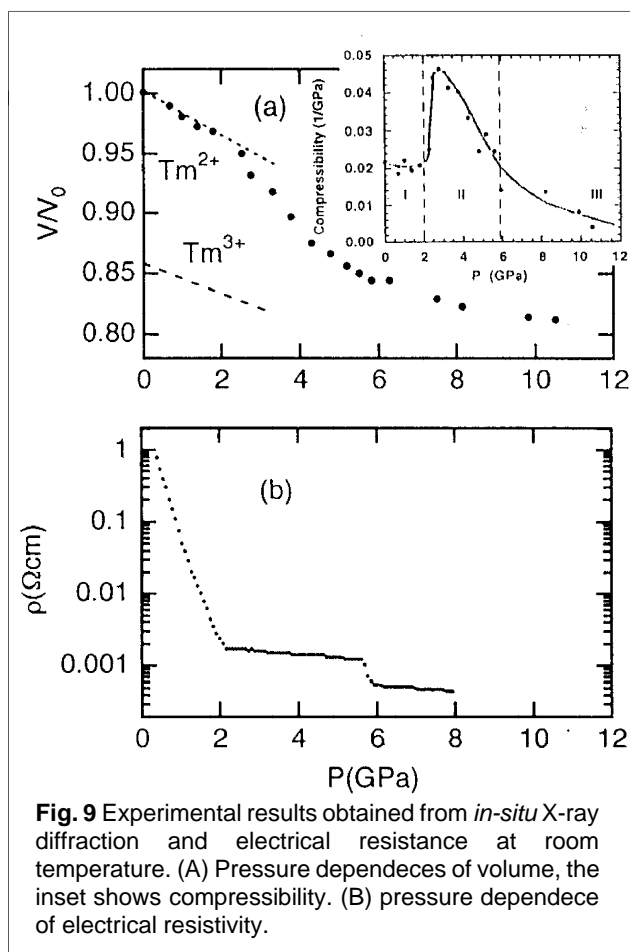
The pressure at low temperature is generally calibrated by the pressure dependence of superconducting transition temperature of bismuth, etc. But X-ray diffraction at low temperature is available in our apparatus, so the pressure calibration can be made more accurately with respect to the optional temperature region.

For the sample temperature, it is normally best to measure it with a thermometer or thermocouple placed next to a sample. In the present case, however, measurement in such a way is extremely difficult due to the small sample chamber under high pressure and the absence of a suitable thermometer being valuable inside the small chamber at high pressure. Therefore a platinum palladium resistance thermometer inserted into a copper holder is installed to the upper anvil of the apparatus, where is the closest place to the sample. Both electrical resistance and temperature measurements are automatically performed on a computer.

### 4. Experimental Example

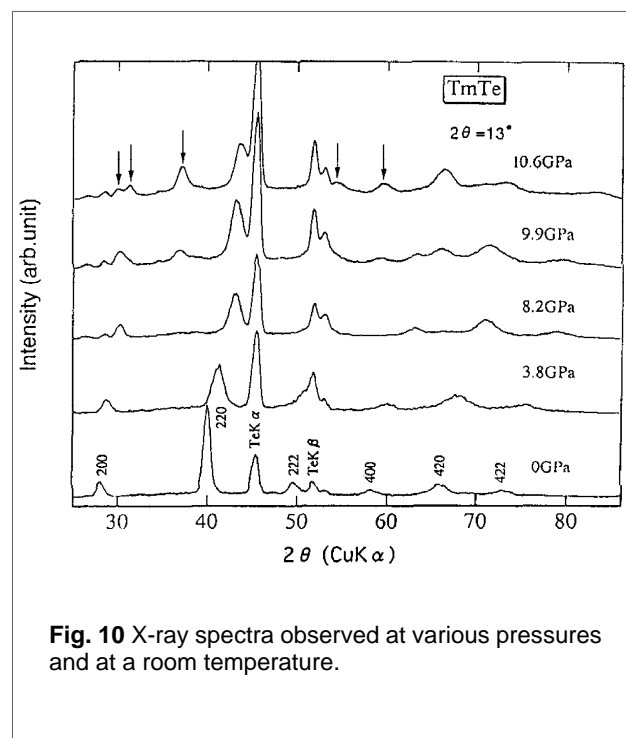
#### — X-ray in situ Observation and Electrical Resistance Measurement of TmTe [4,5]

The Tm monochalcogenides with a NaCl structure display various physical properties depending upon the difference in chalcogen, Te, Se or S. TmTe is a magnetic semiconductor. Its valence band is formed by a filled p band consisting of the 5p orbits of Te, while a vacant d band consisting of the



5d orbitals of Tm become a conduction band, and the  $4f^{13}$  level exists in an energy gap between them. As Tm is a divalent ion, TmTe has a magnetic moment. In other Tm chalcogenides, TmSe is a valence fluctuation material where Tm has an intermediate valence between divalence and trivalence. Further, TmS in which Tm ion is trivalent shows a metallic conductivity with Kondo-like behavior in its electrical resistance. Variation in terms of Tm valence is believed to originate in the different lattice constants, resulting in the change in the electronic properties. TmTe has the largest lattice constant in chalcogenides mentioned above. Accordingly, one can expect to induce similar variations in terms of valence and physical properties by applying pressure to TmTe.

The results of X-ray *in situ* observation and electrical resistance measurement for TmTe are shown in Fig. 9(a), (b). It has been shown from the X-ray diffraction measurement that there are three regions of variation about the pressure dependence of the volume change, as seen in Fig. 9(a) and an inset in it (compressibility of TmTe obtained by differentiating (a)). In the low pressure region, the change of the



volume follows the compressibility of  $Tm^{2+}$ , as indicated by the dotted line. Thus a simple pressure effect may be presumed. In the high pressure region above 2 GPa, the volume reduction rapidly increases to come close to the compression curve of  $Tm^{3+}$ . This is considered to be due to a change in Tm valence from divalence to trivalence. In the further higher pressure region beyond 6 GPa, the pressure dependence of the volume becomes smaller again, and new diffraction lines due to the structure phase transition are observed in a region exceeding 8 GPa, (Fig. 10).

The pressure dependence of the electrical resistance was measured at room temperature. As a result, three regions of variation were also found corresponding with the change in the volume, as shown in Fig. 9(b). In the low pressure region, the electrical resistance decreases exponentially with increasing pressure, indicating the closing process of an energy gap which existed between the  $4f^{13}$  level of Tm and the conduction band. In the intermediate pressure region, the pressure dependence of the electrical resistance becomes smaller considerably. Under pressures beyond 2 GPa, this rapid change seems to be attributed to the vanishing of the energy gap. In a further region of high pressure, the electrical resistance decreases in a discontinuous manner. It is considered to be due to the structure phase transition.

As a typical example, Fig. 11(a) shows the temperature dependence of the electrical resistance at

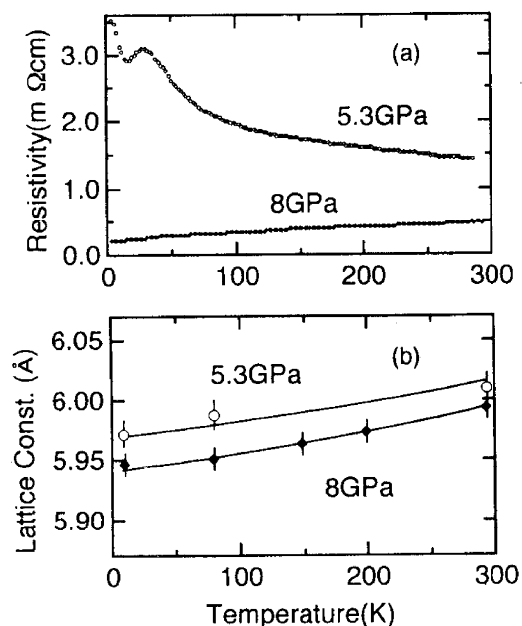


Fig. 11 Experimental results obtained from in-situ X-ray diffraction and electrical resistance as a function of temperature at typical pressures of 5.3 and 8 GPa. (a) Temperature dependences of electrical resistivity. (b) Temperature dependences of lattice constant.

5.3 GPa and 8 GPa. The temperature dependence in an intermediate region of 5.3 GPa is complicated. However the result of X-ray diffraction experiment in this region at low temperature shows that the temperature dependence of the lattice constant decreases monotonically as indicated in Fig. 11 (b). In other words, it is now made clear that the abnormal behavior of the electrical resistance at low temperature is not directly connected to the structure phase transition. From these results through X-ray in situ observation and electrical resistance measurement, we have been able to clarify the valence state of TmTe under high pressure. We have also obtained very interesting results about the metal-insulator transition of  $\text{NiS}_x$ , and  $\text{CuIr}_2(\text{S}_{1-x}\text{Se}_x)_4$ . We would like to report on them in next chance.

## 5. Concluding Remarks

In this paper we have introduced a multipurpose X-ray diffraction apparatus which permits simultaneous measurements of X-ray diffraction and

electrical resistance at low temperature under high pressure. At the present stage we can generate a maximum pressure of 12 GPa (normally up to 9 GPa). We can also get low temperatures down to 5K by newly developed cooling techniques. The simultaneous measurement enables one to obtain information on the physical properties and structure under the same conditions of pressure and temperature. In this sense the system offers many advantages not only, for example, enhancing the reliability of the outcome but providing data on which to decide whether the cause of a physical property change is a peculiarity of the electronic state or a structure phase transition.

Since this is our first attempt which has just been put into practice, we are aware there remain things to be improved in some way or another. Nevertheless, as we are now fairly experienced in operation, we believe our techniques can display high performance in the material research field for the future. More concretely, we are aiming at generating a higher pressure region by improving the anvil top as well as at getting low temperatures below 4 K by pumping the liquid helium. As for the detector, we are planning to execute an angle-dispersive method for X-ray experiment by use of an imaging plate and the like.

## Acknowledgment

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