

# High pressure x-ray diffraction at liquid-helium temperature

S. Endo\* and T. Mitsui

Department of Physics, Faculty of Science, Hokkaido University, Sapporo, Japan

(Received 3 May 1976; in final form, 11 June 1976)

An apparatus for high pressure x-ray diffraction at liquid-He temperature is described that consists of a vessel capable of holding pressure up to 100 kilobar between Bridgman anvils immersed in liquid He in a cryostat. A technique is described for attachment of vacuum-tight beryllium windows to the cryostat. With this apparatus, the superconducting transition temperature of Pb and its dependence on pressure were measured; the pressure was determined from the lattice parameter of NaCl on the basis of the equation of state for NaCl. The result can be used as a low temperature manometer.

## I. INTRODUCTION

For rapid progress in high pressure solid state physics the development of high pressure low temperature techniques is very important. X-ray diffraction can be used to determine thermal contraction and precise lattice constants, which are fundamental quantities for investigating high pressure phenomena in solids. Moreover, it provides meaningful information on pressure-induced phase transitions; the volume change associated with the transitions, and the structural change, at least for materials having relatively simple structures. Various types of cameras have been designed for low temperature diffraction at atmospheric pressure.<sup>1</sup> Previously, the authors reported on diffraction experiments at liquid-N<sub>2</sub> temperature under pressure.<sup>2</sup> In this paper a high pressure camera is described in which the sample is maintained at liquid-He temperature.

## II. APPARATUS

### A. Pressure vessel

Usually a long exposure time is required in experiments of this type. Therefore, a clamp technique was employed to minimize the consumption of He in a cryostat, since with a high pressure press the He consumption is mainly the result of heat conduction through the press column.

A similar type of clamp vessel was described in a previous paper<sup>2</sup> on high pressure x-ray diffraction at liquid-N<sub>2</sub> temperature. Between Bridgman anvils with flats 3.0 mm in diam, pressure up to 100 kilobar or more can be generated by a hydraulic press, and then maintained by means of a locking mechanism. A powdered sample is contained in a hole drilled at the center of a boron-epoxy disk. The diameter of the hole is 0.2 or 0.3 mm. For the passage of incident and diffracted x ray, the vessel has two opposing openings. The vessel is made of copper-beryllium alloy except for the Bridgman anvils which are of tungsten carbide. A difference in thermal contraction of these materials induces a pressure intensification when the vessel is cooled.

### B. Cryostat

Figure 1 illustrates the design of a He cryostat, in which the pressure vessel can be directly immersed. When the cryostat is filled with three liters of liquid He, the sample can be maintained at liquid-He temperature for about 10 h without refilling. This is usually enough time to obtain a diffraction pattern, although the exposure time varies with sample and pressure.

Beryllium sheets used for windows for the outer jacket were attached with epoxy resin, which provided a leak-free seal. However, the Be window of the He container initially leaked upon cooling. After many trials, the following method was adopted. A Be ring 0.5-mm thick and a Cu cylinder were prepared. The cylinder

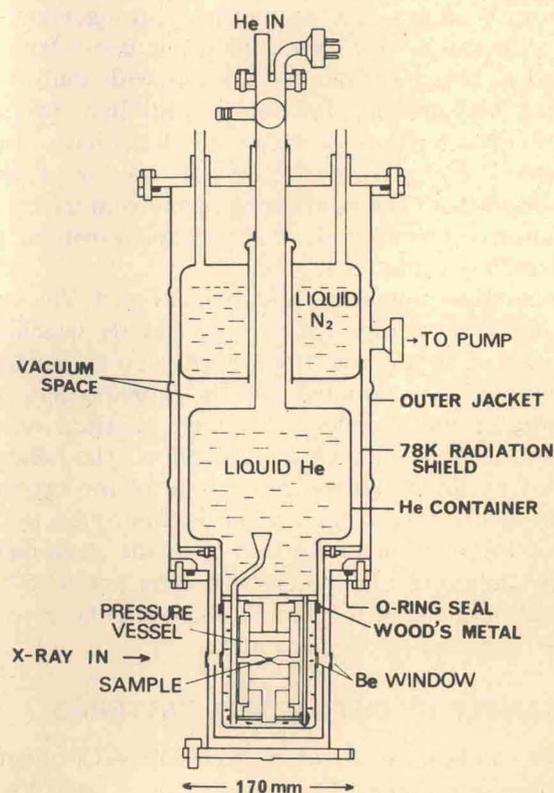


FIG. 1. Internal construction of cryostat for high pressure x-ray diffraction at liquid-He temperature.

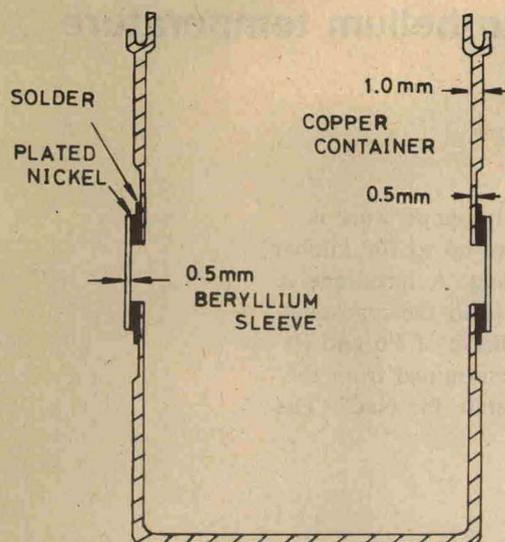


FIG. 2. Method of attaching vacuum-tight Be window to liquid-He container.

was separated to two parts; the upper part and the lower part with a closed bottom. The inside of the Be ring was electroplated with Ni and soldered to the Cu cylinders as shown in Fig. 2. The wall thickness of the Cu cylinder was reduced to 0.5 mm at the joint so that thermal strains on cooling could be greatly relaxed. With Mo radiation the amounts of x-ray absorption by Be windows (total thickness 1.3 mm) and liquid He (88 mm) are 10 and 20%, respectively.

### C. X-ray system

Figure 3 shows the geometrical arrangement for x-ray diffraction. A Guinier focusing geometry was adopted to obtain diffraction patterns with sharp lines and low background. Previously McWhan designed successfully a high pressure camera on the basis of this geometry.<sup>3</sup> A bent quartz crystal was used as a monochromator. The converging beam from the monochromator is 0.5-mm wide at the sample position. The range of  $2\theta$  is within  $\pm 45^\circ$ .

The complete apparatus is shown in Fig. 4. The x-ray generator is a rotating anode type RU-3H which has an output of 60 kV and 100 mA (Rigaku Denki Co.). The cryostat is mounted on the goniometer. The centering of the sample is carefully adjusted on the basis of the maximum x-ray absorption. The height is adjusted by three screws at the base of the cryostat, and the shift in horizontal plane is controlled by the slide of the micrometers attached to the goniometer. In order to avoid the spotty diffraction patterns from the small amount of the sample material, the cryostat can be oscillated by an angle of  $\pm 4^\circ$ .

### III. EXAMPLE OF DIFFRACTION PATTERNS

Figure 5 shows example patterns of NaCl obtained by the present camera. The exposure times were 1 h for the top under 1 bar at room temperature, 2 h for the middle under 1 bar at liquid-He temperature, and 3 h

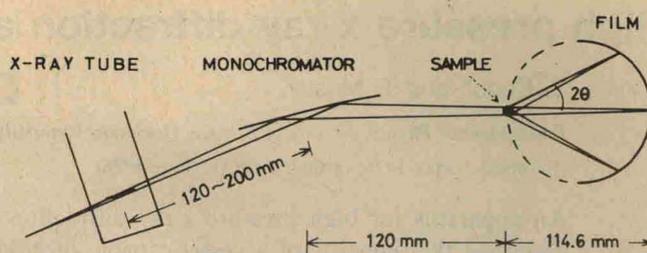


FIG. 3. Guinier-type focusing geometry for the present apparatus.

for the bottom under 60 kilobar at liquid-He temperature, respectively. The shifting of diffraction lines which results from the lattice contraction is clearly observed. The splitting of the  $K\alpha$  doublet is seen on the right-hand side of all the patterns.

### IV. MEASUREMENT OF PRESSURE GRADIENT IN THE BORON-EPOXY CELL

By measuring the values of lattice parameter of NaCl distributed in a radial direction of the boron-epoxy cell, the gradients of the pressure on the anvil were determined. As shown in Fig. 6, when the center is pressed to 90 kilobar, the pressure at 0.7 mm away from the center drops to as low as 20 kilobar.

### V. PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF Pb

One of the most difficult problems in high pressure studies at low temperature is the precise determina-

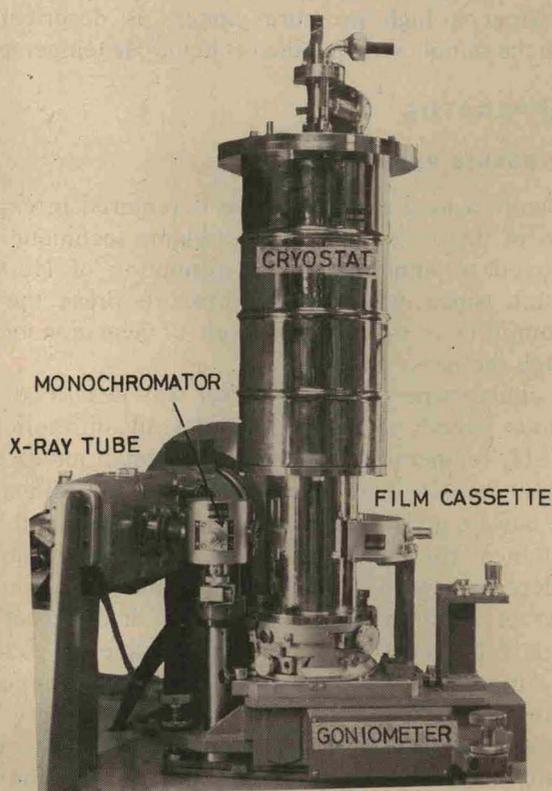
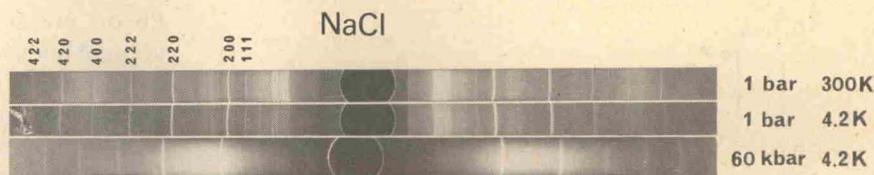


FIG. 4. High pressure x-ray diffraction apparatus for use at liquid-He temperature.

FIG. 5. Powder patterns of NaCl under various conditions. Five diffraction lines inside NaCl 111 line emanate from "amorphous" boron cell material.



tion of the pressure. The calibration at room temperature can not be adopted directly at low temperature because of thermal contraction and changes in elastic constants of the sample and the pressure transmitting material. For this purpose, as a conventional manometer, the pressure dependence of the superconducting transition temperature,  $T_c(P)$  of metals has been frequently used. Investigations of  $T_c(P)$  of metals such as Pb, Sn, and In, have been carried out.<sup>4</sup> In these studies, however, only indirect methods have been used for the determination of the pressure.

At elevated temperature the equation of state for alkali halides such as NaCl and CsCl was calculated by Decker,<sup>5,6</sup> and has been used as the most reliable scale of pressure. In this study,  $T_c(P)$  of Pb has been determined by referring to the equation of state for NaCl. In other words, the lattice parameter of NaCl under high pressure was measured at low temperature by use of the above mentioned x-ray camera.

#### A. Pressure determination at low temperature

Decker's calculation of the equation of state for NaCl at elevated temperature is based on the vibrational Mie-Grüneisen equation of state,

$$P = - \frac{d\Phi(V)}{dV} + \frac{\gamma_E}{V} E_v(V, T),$$

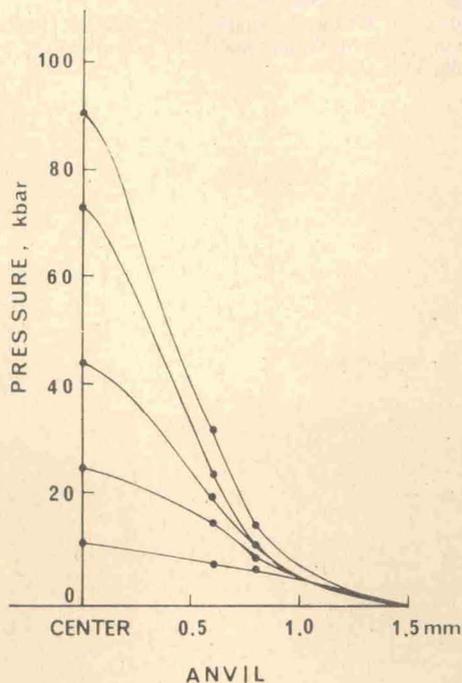


FIG. 6. Radial pressure distribution in the boron-epoxy cell with 3.0-mm diam at room temperature.

where  $P$  is the pressure,  $\Phi(V)$  the potential energy due to the static lattice,  $E_v(V, T)$  the energy due to the lattice vibrations including the zero-point vibrations,  $V$  the volume, and  $T$  the temperature.  $\gamma_E$  is the Grüneisen parameter, but is not identical with  $\gamma$  defined by the Grüneisen rule.<sup>7,8</sup> At low temperature,  $\gamma_E$  is a function of both volume and temperature. Therefore, Decker's assumption that the Grüneisen parameter is a function of volume only is not valid at low temperature. However, Pautamo's calculation of  $\gamma_E$  for NaCl at atmospheric pressure indicates that  $\gamma_E$  varies much less with temperature than  $\gamma$ .<sup>8</sup> The difference between  $\gamma_E$  and  $\gamma_D$  (suffix  $D$  means the parameter used in Decker's calculation) is much smaller than that between  $\gamma_E$  and  $\gamma$ . It is difficult to calculate theoretical values of  $\gamma_E$  at low temperature under pressure. The use of  $\gamma_D$  instead of  $\gamma_E$  has a direct bearing on the term  $(\gamma_E/V)E_v$  in Mie-Grüneisen equation. Assuming that the difference between  $\gamma_E$  and  $\gamma_D$  at atmospheric pressure holds equally at high pressure, the pressure obtained by extension of Decker's calculation using  $\gamma_D$  is low by the amount of 0.6 kilobar at 100 kilobar and 4.2 K compared with that obtained by using  $\gamma_E$ . This amount is almost negligible, when considering the uncertainty in pressure determination,  $\pm 1$  kilobar, resulting from the uncertainty in the present measurement of  $V/V_0$  for NaCl. Then Decker's calculation extended to 4.2 K was adopted as a reasonable scale in the present study. The differences in the pressures at 4.2 K and neighboring temperatures are entirely negligible.

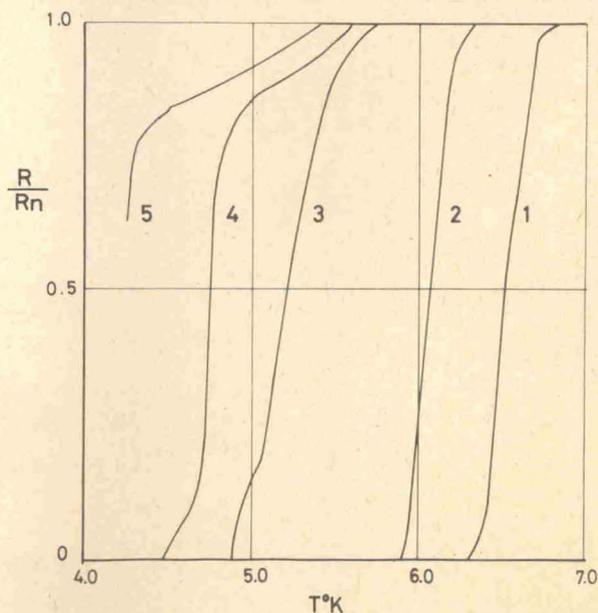


FIG. 7. Curves of the superconducting transition in Pb at various pressures  $P$  (kilobar): 1—7.0, 2—24.7, 3—36.0, 4—43.4, 5—53.2.

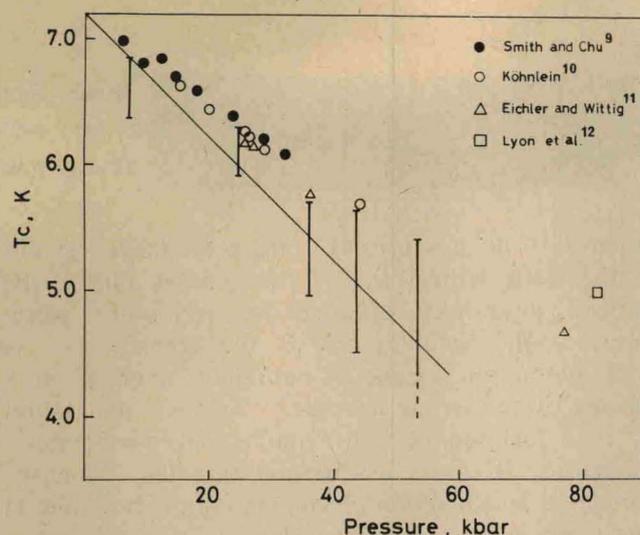


FIG. 8. Plot of  $T_c(P)$  for Pb. Vertical lines indicate the result of the present work.

## B. Experimental and results

In addition to the lattice parameter measurements of NaCl at 4.2 K, the electrical resistance of Pb was measured on spontaneous warming in order to determine the transition temperature. A wire made of Pb was imbedded vertically in the NaCl powder contained in the boron-epoxy disk. The electrical resistance was measured across the anvils with a double bridge. Temperature was measured with a germanium resistor attached to the lower anvil. The warming rate was 0.8 K/h up to 5.6 K, and 6.5 K/h above 5.6 K.

Figure 7 indicates the dependence of the relative electrical resistance of Pb on temperature under various pressure. Curve 5 for 53.2 kilobar shows the result above 4.2 K. The curves become less steep as the pressure increases. This is mainly attributed to the gradient of pressure throughout the sample. Figure 8 shows the dependence of the transition temperature of

Pb on pressure, which is obtained from Fig 7. The vertical lines indicate the probable ranges of the present experimental result. Data by Smith *et al.* and the data quoted by them<sup>4</sup> are also plotted in this figure. The present values are significantly lower than the others. The reason for this is not clear, but may be due to the difference in methods for the pressure determination at low temperature. Smith and Chu's measurement<sup>9</sup> was based on the change of  $T_c(P)$  of a Sn manometer, and Köhnlein's<sup>10</sup> was made using a strain-gauge technique. Eichler and Wittig<sup>11</sup> measured  $T_c$  at the transition points in Bi and Tl. In the case of Bridgman anvils used by all of them, a pressure gradient along the anvil at low temperature may be different from that at room temperature because of the decrease in plasticity of the pressure medium. A detailed redetermination in a hydrostatic environment seems to be necessary.

## ACKNOWLEDGMENTS

The authors would like to thank Rigaku Denki Co. and Rikensha Co. for help in making the apparatus, and Nippon Gaishi Co. for technical assistance for attaching the Be window to the He container.

\* Present address: Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Japan.

<sup>1</sup> See, for example, C. S. Barrett and T. B. Massalski, *Structure of Metals*, 3rd ed. (McGraw-Hill, New York, 1966), pp. 122-123.

<sup>2</sup> S. Endo, K. Yamakawa, and T. Mitsui, *Jpn. J. Appl. Phys.* **12**, 1251 (1973).

<sup>3</sup> D. B. McWhan, *J. Appl. Phys.* **38**, 347 (1967).

<sup>4</sup> See, for example, T. F. Smith, C. W. Chu, and M. B. Maple, *Cryogenics* **9**, 53 (1969).

<sup>5</sup> D. L. Decker, *J. Appl. Phys.* **36**, 157 (1965).

<sup>6</sup> D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971).

<sup>7</sup> F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids* **23**, 395 (1962).

<sup>8</sup> Y. Pautamo, *Ann. Acad. Sci. Fenn. A* **6**, 1 (1963).

<sup>9</sup> T. F. Smith and C. W. Chu, *Phys. Rev.* **159**, 353 (1967).

<sup>10</sup> D. Köhnlein, *Z. Phys.* **208**, 142 (1968).

<sup>11</sup> A. Eichler and J. Wittig, *Z. Angew. Phys.* **25**, 319 (1968).

<sup>12</sup> D. N. Lyon, D. B. McWhan, and A. L. Stevens, *Rev. Sci. Instrum.* **38**, 1324 (1967).