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Clamp Type High Pressure Apparatus Using Small Bridgman Anvil at Low Temperature

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High pressure apparatus at liquid helium temperature is built. It is a high pressure cell of clamp type using small Bridgman anvil (4 mm face) geometry. The pressure is applied to a sample using a standard hydraulic press and clamped by means of three bolts at room temperature, then the cell is cooled down to low temperature. The pressure is calibrated by means of the phase transition of Bi, Tl and Sn at room temperature, and pressure dependence of superconductive transition temperature of tin at low temperature which is measured by means of the electrical resistance and a.c. mutual inductance bridge.

§ 1. Introduction

In the field of solid state physics, investigations at high pressure and low temperature have been made and these investigations are mainly P. V. T. relations of solidified gases and the measurement of the effect of pressure on the superconductive transition. For researching high pressure effects at low temperature, two directions chiefly exist. One is a study of initial slope of pressure dependence in physical properties under hydrostatic pressure condition below 10 kbar, and the other is a study under very high pressure. In the latter case the hydrostatic pressure condition is poor than the former. For the former study, a direct piston displacement apparatus[1] or a helium gas pressure apparatus[2] have been used. The direct piston displacement apparatus is a simple device of generating pressure less than 20 kbar at low temperature, which has an advantage for applying a continuously variable force to the experimental piston. Then pressure can be controlled by a hydraulic press at room temperature. Because of this reason, the apparatus becomes large and consumes a lot of liquid helium (about 1 *l*/h). Moreover, it cannot cool down to temperature lower than 2K because of its large heat capacity and large heat conduction from the outside.[3]

Pressure in the gas system can be also varied continuously up to the freezing pressure of the gas, but this is hazardous to work with. The pressure range of the gas system is quite limited less than 10 kbar at low temperature.

The latter very high pressure device was originally made by a so-called 'fixed clamp' technique of Chester and Jones[4] and has been developed by Buckel and Wittig.[5] A thin sample was squeezed between two anvils together at room temperature and subsequently clamped. The clamped anvils were detached from the hydraulic press system, and cooled to low temperature. This fixed clamp method of producing very high pressure suffers from the defect that the pressure cannot be varied continuously at low temperature. To change the pressure in the sample, the clamp must be reset at room temperature. However, the absence of heavy external connections means that the heat leaks into the experimental cryostat can be kept very small. By this method, Buckel and Wittig found the new modification of superconductor of Si and Ge which are semiconductors at normal pressure. These discoveries seem to suggest that the other non-superconductive materials may become superconductors at high pressure. It is very interest whether or not, for example, all alkali metals become superconductors under the condition of high pressure and low temperature.

In order to study properties of solid under the extreme condition of high pressure and low temperature, especially higher than 100 kbar and lower than 0.1 K, we have built a high pressure clamp type apparatus at low temperature which accepts a small Bridgman anvil. This cell is improved on the Wittig's type. At the same time we developed a

technique of the measurement of a.c. magnetic susceptibility. The pressure in this high pressure cell is calibrated by the phase transition of Bi I-II, III-V, Tl I-II and Sn I-II at room temperature, and by the pressure dependence of superconductive transition temperature of tin at low temperature. In this paper, the design of the pressure apparatus, its pressure calibration and the methods in measuring of the resistance and susceptibility are discussed.

§ 2. Clamp Type High Pressure Apparatus

Clamp type high pressure apparatus which accepts a small Bridgman anvil is most convenient to obtain the extreme conditions of lower temperature and higher pressure. Furthermore, this apparatus can avoid excessive helium consumption.

Thus we have built a clamp type cell used a small Bridgman anvil (4.0 mm face) geometry which is made from tungsten carbide. This has mainly two advantages as follows; the first is to have used the flange type for clamping mechanism and the second is to have developed an a.c. mutual inductance method for measuring the superconductive transition temperature using weakly ferromagnetic tungsten carbide anvil.

Wittig[6] had used a mechanism which clamped a Bridgman anvil tightly each other with an attached screw nut.

At first, we had used Wittig's mechanism. But in that way, we had often troubled to break of lead wires during the clamping process because the lead wires are twisted when the screw nut is tightened to clamp. Therefore, we have improved Wittig's cell in several points. The high pressure cryostat is shown in Fig. 1. As shown in Figure 2, to clamp a sample, two flanges and three bolts are used. This type is convenient to exchange the sample and is free from the twist of lead wires. Moreover, using this cell, one can adopt an a.c. method of a measurement which means a no-lead wire method so it is convenient to avoid the trouble of the lead wire discussed above. The material of the high pressure apparatus at low temperature is one of serious problem. Most steels become brittle at low temperature. In general, steels with low carbon and high nickel content (austenitic stainless steel) are sufficiently ductile at low temper-

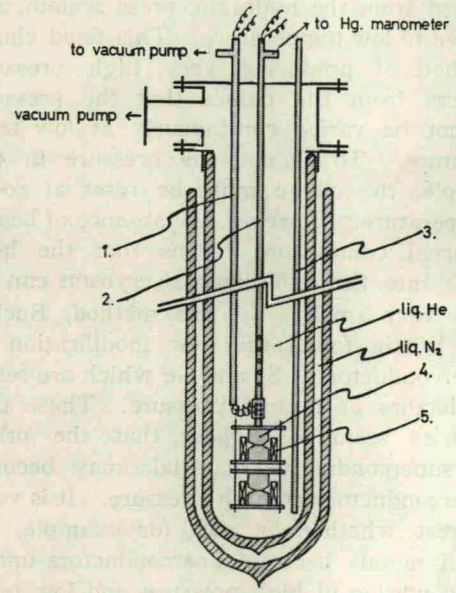

Fig. 1. High pressure cryostat.
1. Vacuum stainless steel tube. Electrical lead wires for measuring the a.c. mutual inductance pass through this tube.
2. Stainless steel tube which supports the high pressure clamp apparatus. Electrical lead wires for the d.c. measurement pass through this tube.
3. Inlet for the liquid helium.
4. Tungsten carbide anvil.
5. Measuring coil.

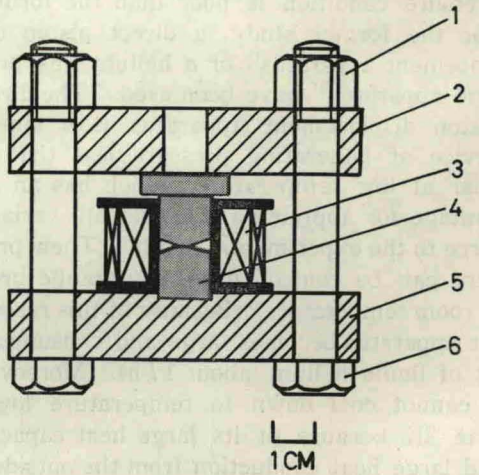

Fig. 2. High pressure clamp apparatus.
1. Fixing nut.
2. Upper flange.
3. Measuring coil.
4. Tungsten carbide anvil.
5. Lower flange.
6. Clamping nut.

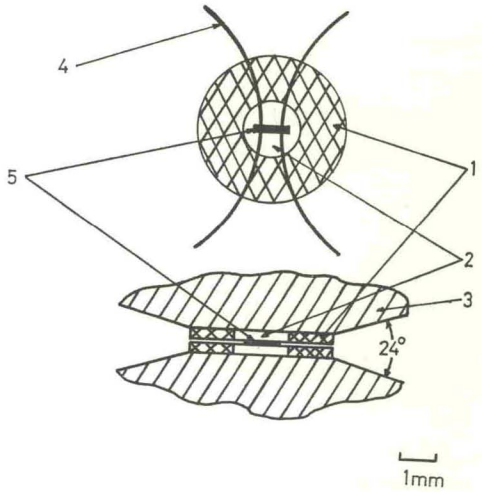

Fig. 3. Sample assembly for d.c. method.
1. Pyrophyllite ring.
2. Talc disk.
3. Tungsten carbide anvil.
4. Lead wire.
5. Sample.

ature. Then, two flanges and a clamping bolts are made from the 18-8 stainless steel (SUS 27). Two flanges are 80 mm in diameter and 15 mm in thickness. Three bolts are 10 mm in diameter and 120 mm in length.

The sample assembly is shown in Fig. 3. The pyrophyllite ring (4.0 mm i.d., 1.5 mm i.d., 0.15 mm thick) is heated at 650°C, for 30 minutes in order to increase the hardness, which is fixed with an insulating cement to a face of the anvil. A specimen is placed in the talc disc (1.5 mm o.d., 0.15 mm thick). The talc disc is made from pressed powder of talc. The talc is much more plastic than pyrophyllite and thus produces sufficient uniformity in the generated pressure. The consumption of liquid helium in this clamp type cell is only 0.3 *l*/h. When the high pressure apparatus is cooled to low temperature, we may expect the pressure in the sample to remain homogeneous throughout, if the sample and pressure transmitting medium shrink isotropically.

§ 3. Measurement of Electrical Resistance and Magnetic Susceptibility

The electrical resistance is measured by a conventional d.c. four leads method. In a resistance measurement, however, the most serious problem is the break of a lead wire because of the extrusion of the talc and

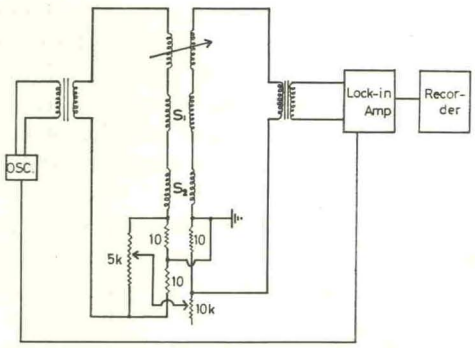

Fig. 4. Schematic diagram of a.c. mutual inductance measurement.

pyrophyllite under pressure. Therefore, a no-lead wire method is convenient for the experiment. We have developed a method of an a.c. magnetic susceptibility measurement[7] by means of an a.c. mutual inductance bridge operated 230 H_z. Usually, in the experiment of a magnetic measurement under pressure, the alumina anvil had been used instead of the tungsten carbide anvil because it is weakly ferromagnetic. But we have used the tungsten carbide anvil (11 mm in height, 12 mm in diameter, 4 mm in face) because of obtaining very high pressure. Although it may make less sensitive than using the alumina anvil, we could gain enough sensitivity to detect the superconductive transition of the sample as small as $1.0\times0.5\times0.03$ in its size.

Figure 4 shows the schematic diagram of the a.c. mutual inductance measurement. The sample is represented by S_1 and S_2 and usually, S_1 is the non-compressed sample and S_2 is under compression. The primary and secondary coils are wounded in 900 turns and 1500 turns (Cu wire, 0.14 mm in diameter), respectively.

The direction of the primary coil wounded around S_1 and S_2 is the same one but the secondary coils are wounded inversely to compensate each other. S_1 and S_2 are placed in the high pressure cell which is just the same form each other in order to cancel the magnetic effect of the ferromagnetic tungsten carbide anvil.

The a.c. signal of 230 H_z and about 5 V rms amplitude is applied to the primary of the measuring coil and rms primary current is typically about 15 mA. The inductive unbalance voltage in the secondary circuit can

be cancelled by the small variable inductor. A variable voltage drived from the resistive network is interjected directly into the secondary circuit and serves to cancel a resistive unbalance. The unbalance voltage is amplified by a lock-in amplifier and made available for detection.

In operation, the unbalance voltage is approximately nulled by the inductive and resistive network discussed above. The change of a.c. mutual inductance caused by the superconductive transition is then recorded by an X-Y recorder. The X axis records the temperature. The balance of the mutual inductance bridge is sensitive in a resistive change of the measuring coil. This lead wires for measuring the a.c. mutual inductance are passed through the vacuum tube.

§ 4. Pressure Calibration

The pressure at room temperature is calibrated using several fixed points which are the phase transition of Bi I-II, III-V, Tl I-II and Sn I-II, by means of the d.c. method. The pressure scale is based on N. B. S. Symposium Scale on 1968 (Table I).[8]

The pressure is applied to a sample using a standard hydraulic press at room temperature. The resistive change is recorded directly by a d.c. method with slowly increasing the pressure of hydraulic press. Fig. 5 shows the load-resistance curve in Bi at room temperature. Figure 6 shows the pressure-load calibration curve at room temperature, using small Bridgman anvil (4.0 mm face) geometry.

Table I. N. B. S. Symposium Scale (1968).[8]

	Bi I-II	Tl I-II	Bi III-V	Sn I-II
P. (kb)	25.50	36.7±0.3	77±3	100±6

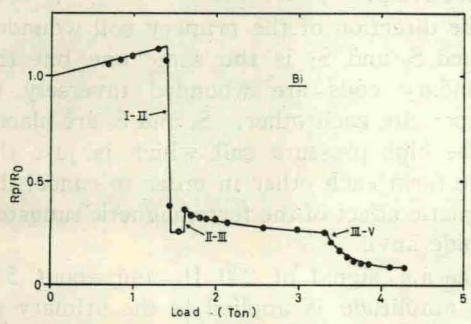

Fig. 5. Load-resistance curve in Bi at room temperature using a small Bridgman anvil (4.0 mm face) geometry.

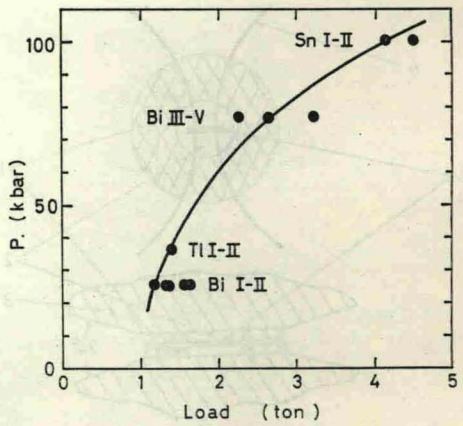

Fig. 6. Pressure-load calibration curve at room temperature using a small Bridgman anvil (4.0 mm face) geometry.

The clamp is carried out in following ways. At first, the desired pressure has been applied to a sample by a hydraulic press and the pressure is monitored by means of recording the electrical resistance of the sample. This pressure is clamped by means of three bolts, and the clamped cell is detached from the hydraulic press. At this time, the pressure relaxation is often caused by the imperfect binding of clamping bolts. Therefore, the clamp is done usually at 5 percent extra pressure. But, the final check of clamped pressure is done with measuring the resistance of the sample.

A pressure manometer at low temperature is readily available in the form of a number of superconductors whose transition temperature (T_c) are sufficiently sensitive to the change of pressure. Swenson[9] proposed a particularly useful pressure scale up to 10 kbar using a tin manometer. The relationship is given in polynomial form by

$$\Delta T_c = T_c(P) - T_c(0) = -4.7\times10^{-2}P + 3.6\times10^{-4}P^2 \qquad (1)$$

with pressure P in kbar.

Swenson's relationship between the tin superconductive transition temperature and pressure (eq. 1) is not valid at pressure greater than 10 kbar. However, Smith *et al.*[10] avoided the limitations up to 100 kbar by adopting the relationship derived from the theory of Birch,

$$P = A(Z^7 - Z^5)[1 - B(Z^2 - 1)] \qquad (2)$$

where

$$A=\frac{3B_k}{2}, \quad B=3-\frac{3Bk'}{4},$$

and

$$Z=\left(\frac{V_0}{V}\right)^{1/3}.$$

V_0 is the volume at zero pressure and V the volume at pressure P. B_k is the isothermal bulk modulus and B_k' is its pressure derivative at zero pressure. At first, the volume change over a considerable pressure range is calculated from the use of appropriate B_k and B_k' using eq. (2). Here, they assumed that the linear variation of T_c with the volume change found from Swenson's data continues to hold up to 100 kbar. A least squares linear fit of ΔT_c to $\Delta V/V_0$ was then made to give $\gamma_s=(\partial \ln T_c/\partial \ln V)_{P=0}$. Having derived γ_s this may then be used to generate volume changes appropriate to a given change of T_c, which in turn may be substituted into the eq. (2) to obtain the corresponding pressures. In this way, the change of superconductive transition temperature as a function of pressure for tin was computed for 1 mdeg changes in T_c. We have used Smith *et al.*'s tin scale discussed above as a pressure manometer at low temperature. Then tin sample of 99.9% purity is rolled to a thickness of 0.03 mm and is annealed at 150°C, for 2 hours. Figure 7 shows the superconductive transition curve in each clamp load. The superconductive transition temperature is determined from the vapor pressure of liquid helium. The transition temperature is taken from the midpoint of the transition. The transitions are fairly sharp as shown in Fig. 7. From the sharpness of observed superconductive transitions, we considered that the homogeneity of pressure transmitting medium is fairly good. Figure 8 shows the change of superconductive transition temperature of tin *vs.* the clamp load. The agreement between the resistance and susceptibility measurements is fairly good. From these results, we were taken the pressure calibration curve as shown in Fig. 9.

The effects of differential thermal contraction coupled with changes in elastic properties have caused the pressure to drop appreciably with temperature. At low temperature, the pressure loss is about 25%.

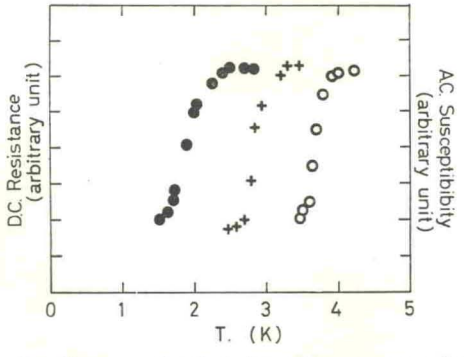

Fig. 7. Superconductive transition curve of tin at different clamp load.
○: non-compressed....a.c. method.
+: 0.8 ton load .....d.c. method.
●: 2.6 ton load .....a.c. method.

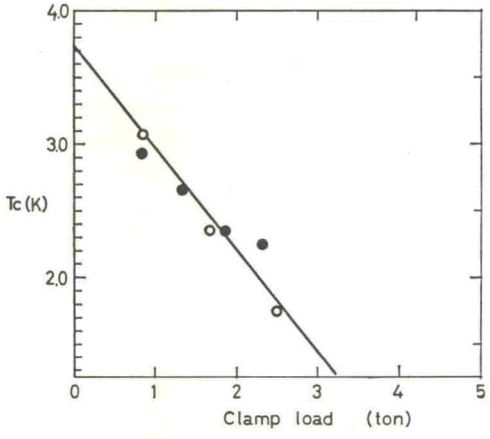

Fig. 8. Load dependence of superconductive transition temperature of tin.
●: d.c. resistance measurement.
○: a.c. susceptibility measurement.

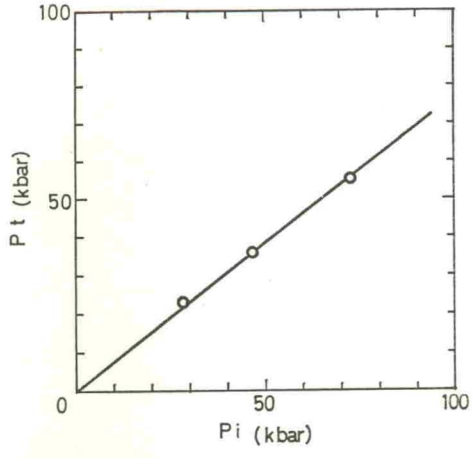

Fig. 9. Pressure calibration curve in the small Bridgman anvil (4.0 mm face) geometry;
P_i is the clamped pressure at room temperature.
P_t in the generated pressure at low temperature.

§ 5. Conclusion

The high pressure apparatus of clamp type was built. This apparatus was convenient to the high pressure experiment at low temperature because the experimental procedure is very simple and the consumption of liquid helium is very little because of its small heat capacity, that is 0.3 *l*/h. We have experimented the d.c. electrical resistance and a.c. mutual inductance measurement which are enough to detect the pressure dependence of the superconductive transition temperature of tin using the ferromagnetic tungsten carbide anvil (4 mm face) geometry. At room temperature, the pressure was generated up to 100 kbar using the small Bridgman anvil (4 mm face) geometry.

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