

High pressure techniques at low temperatures

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Abstract. The article reviews the experimental techniques used in high pressure-low temperature investigations to study a variety of physico-chemical phenomena. The general principles of producing high pressures at low temperatures, the methods of measuring P and T, the materials used for construction and the diamond anvil cell (DAC) are briefly given first. Specific pieces of apparatus to measure the mechanical properties, phase equilibria, thermal properties, electrical properties, magnetic phenomena, optical and Raman/IR spectroscopic behaviour as well as Mössbauer spectra are then discussed. While instrumentation is the main emphasis of the article, a few illustrative examples of interesting observations are also indicated. Over 250 current papers are cited.

Keywords. High pressure techniques; low temperatures; diamond anvil cell; mechanical properties; phase equilibria; thermal properties; electrical properties; magnetic phenomena; Raman spectra; Mössbauer spectra; instrumentation.

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1. Introduction

The study of the behaviour of materials at high pressures and low temperatures has been useful not only in understanding the properties of these materials but also in the observation of new features of the physicochemical properties. It is now believed that almost all materials will become metallic at sufficiently high pressures; therefore a combination of high pressures with low temperatures is a logical step in pursuing this phenomenon. Many superconductors have been discovered at high pressures and low temperatures. Pressure as a thermodynamic parameter and as a means of perturbing the symmetry of the system has a unique role and many of the phenomena are clearly studied only at low temperatures. For instance the study of the Fermi surface of metals at high pressures has given new insights. However progress in these directions has been hampered by the experimental difficulties in performing these measurements which combine two already difficult techniques (Swenson 1960; Stewart 1962; Brandt and Ginzburg 1965, 1969; Dugdale 1969; Paureau 1977; Chu and Woolam 1978). Nevertheless the fact that a variety of new phenomena and investigations can be performed under the simultaneous application of high pressures and low temperatures makes it desirable to review the various experimental techniques used in these studies. Inevitably some indications of the physical phenomena thrown up in these investigations have to be pointed out briefly in this review. Equally inevitable are omissions

caused by the conference deadlines and the consequent inadequacy in the scrutiny of literature.

1.1 General principles of high pressure generation at low temperatures

The experiments of Simon *et al* (1930) in exploring the melting curves of the permanent gases upto 0.5 GPa could be said to be the beginning of the modern phase of high pressure-low temperature research. Bridgman (1932) studied the pressure dependence of electrical resistivity upto 0.75 GPa with helium as a pressure transmitting medium. A major interest in the 1930's was the investigations of the possible existence of a solid-fluid critical point analogous to that possessed by well-known liquid-vapour transitions. A solidified gas, in particular helium, was thought to be the most promising substance for the observation of such a phenomenon.

In 1940's Lazarev and Kan (1944) developed perhaps the simplest high pressure-low temperature apparatus (called the ice-bomb technique) using the phenomena of the ice I-III water triple point transformations (Bridgman 1937). The pressure here is produced by the solidification of water in a bomb of constant volume. A maximum pressure of about 0.17 GPa at 4.2 K is achieved. Chester and Jones (1953) introduced the important clamp technique in which by mechanical methods the pressure is locked in at room temperature and the cell is cooled down to helium temperatures. The cell can be either of the piston-cylinder design (figure 1) or of the Bridgman-anvil type (figure 11). In the original apparatus a maximum pressure of 4 GPa at 4.2 K was achieved with a Bridgman-anvil cell (Chester and Jones 1953). Subsequently techniques in which the pressure can also be changed at low temperatures were developed (Buckel and Gey 1963; Berman and Brandt 1968; Syassen *et al* 1971; Alymov *et al* 1972). In the last decade, the diamond-anvil cell has proved to be very suitable for producing high pressures at very low temperatures (Jayaraman 1983).

1.2 Materials used for high pressure-low temperature generation

The main requirements of a high pressure-low temperature system are: (i) A suitable material to withstand the stresses involved, especially at low temperatures. (ii) A

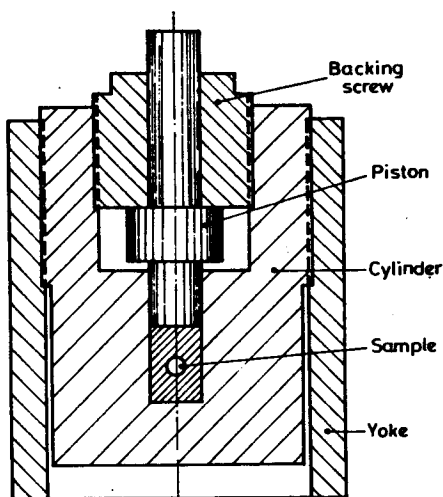


Figure 1. Clamp cell of the piston-cylinder type. The high pressure is generated by advancing the piston and locked by tightening the backing screw.

pressure-transmitting medium which remains soft at low temperatures, so that the pressure is hydrostatic. It must also be electrically insulating and chemically inert. (iii) A mechanism for sealing at high pressures and at low temperatures. Care must be taken to see that the materials are devoid of defects, blow holes, etc.

The most commonly used materials for the pressure vessels are Be-Cu alloys and stainless steels which have sufficient mechanical strength at low temperatures. These materials also have the added advantage of being nonmagnetic. Tungsten carbide has been successfully employed in piston-cylinder devices, upto a pressure of 2 GPa and at liquid helium temperatures. Nuclear orientation experiments upto 2 GPa pressure and temperatures down to 8 mK have been performed by using pressure cells made of Be-Cu alloy connected to dilution refrigerators (Benoit *et al* 1974; Ribault and Benoit 1978). Webb *et al* (1976) used a diamond anvil cell of 0.5 mm diameter, developing a pressure of 10 GPa down to 30 mK temperatures. The use of diamond anvil cell at very low temperature will be discussed in a later section of this review.

1.3 Pressure-transmitting medium

Pressure experiments which demand truly hydrostatic conditions become very difficult at temperatures below 77 K and pressures above 2 GPa. The problem arises because the plasticity of the pressure-transmitting medium decreases sharply on lowering the temperature. Various pressure transmitting media have been used. Lazarev and Kan (1944) used water which is filled in the high pressure bomb at room temperature, sealed and the bomb is cooled. The pressure is generated by the expansion of water, freezing under approximately constant volume conditions. The maximum pressure obtained in this system is limited to 0.17 GPa at liquid helium temperature, being controlled by the phase diagram of water. Unfortunately, the uniformity of pressure is not very good. In the clamp-bomb method (Itskevich 1964) a pressure of 1.5 GPa was achieved, a mixture of oil-kerosene being used as the pressure-transmitting medium. Stewart and Swenson (1954) developed a method in which liquid and solid helium is directly compressed in a piston-cylinder apparatus at 4.2 K (Schirber 1970). Porowski *et al* (1977) improved Stewart's method with a better sealing of the piston, which permits the temperature to be changed over a wide range and also the cycling of pressure. Normally, talc and teflon are used as pressure-transmitting media instead of hydrogen or helium gas. This is because the gas medium is hazardous to work with and the pressure system with a gas medium is complex; working with hydrogen (or helium) is sometimes hazardous. Hence a solid pressure-transmitting medium is preferred and talc and teflon are found to be very satisfactory for this purpose (Bradley 1969; Giardini and Lloyd 1963; Lloyd and Giardini 1964; Bradley 1966, 1969a, 1969b; Lloyd 1971; Paureau 1977; Kelm 1978; Chu and Woolam 1978; Timmerhaus and Barber 1979; Vodar and Marteau 1980; Schilling and Shelton 1981). The use of gases like helium in a diamond anvil cell at low temperatures will be discussed later.

1.4 Calibration

The simplest method of estimating the pressure in an apparatus is to calculate the force over area and correct for friction. The variations of superconducting transition temperatures and critical fields as a function of pressure are available for a large

number of metals (For reviews see Bowen 1958; Jennings and Swenson 1958; Brandt and Ginsburg 1965; Levy and Olsen 1965). A manometer using the transition temperature of pure tin may be used to give the pressure accurate to within a few percent over the pressure range 10^5 Pa to 1 GPa. Jennings and Swenson (1958) found the equation $T_c = 3.732 - 4.88 \times 10^{-5} P + 3.8 \times 10^{-10} P^2$ where P is in bars (1 bar = 10^5 Pa). Levy and Olsen (1965) placed two specimens in the experimental cavity using one of known dT_c/dP as a manometer, and relied on the plasticity of the specimens at the pressures used to ensure a homogeneous and equal pressure for the test specimen and the manometric specimen. Eiling *et al* (1981) demonstrated that Pb and Sn are ideally suited for use as accurate resistive manometers, enabling a reliable continuous determination of pressure (0–10 GPa) over a wide range of temperature (1–300 K). The other simple ways of calibrating pressure at low temperature are to study the pressure induced polymorphic phase transitions in Bi, Yb, Tl at different temperatures (Ilna and Itskevich 1967, 1970; Stager and Drickamer 1963; Homan 1975; Compy 1970; Lyon *et al* 1967; Parthasarathy *et al* 1984). This method is rather time-consuming in the case of clamp-type of cells. Hence for a clamp type cell the pressure dependence of superconducting temperatures of metals is much more convenient and for the continuous pressure and temperature changing system the phase transition of the elements at low temperatures is found to be most suitable for pressure calibration. For measuring the temperature between 4.2 and 300 K, chromel/alumel thermocouple is ideal because of the small shift in thermo-emf and the high reproducibility under hydrostatic pressure upto 2.2 GPa (Diatschenko and Chu 1975; Lazarus *et al* 1971). Rhodium plus 0.5 at. % iron against chromel is a new material (Guy *et al* 1986).

When cooled the pressure in a clamped cell changes slightly. For determining this pressure variation in a clamped cell at low temperature, one uses the electrical resistivity of metals as the temperature is lowered, e.g. lead (Bandyopadhyay *et al* 1980; Eiling *et al* 1981) or manganin (Fujiwara *et al* 1980; Brandt *et al* 1976; Itskevich 1964; Thompson 1984; Sinha and Srinivasan 1983). The pressure calibration of the diamond anvil cell at low temperature will be discussed in the next section.

2. Diamond anvil cell at low temperature

The diamond anvil cell (DAC) is capable of generating 2.5 megabar pressures at very low temperatures (Goettel *et al* 1985) and its development is a major step in modern high pressure research. The principles underlying the DAC, the pressure calibration, and the application of DAC in physical investigations have been reviewed by Block and Piermarini (1976), Jayaraman (1983) and Bundy (1986a). Since the DAC is small and compact the simplest method of direct immersion in a cryogenic fluid N_2 , O_2 has been used. However, operation at liquid helium temperatures requires a specially designed cryostat. Webb *et al* (1976) designed an apparatus for pressures up to 10 GPa and temperature down to 30 mK, which uses a Bassett type cell (Bassett *et al* 1967; Jayaraman 1972) in a He^3 - He^4 dilution refrigerator. In this, pressure can be changed from outside by applying He^4 gas pressure to a chamber with bellows, which in turn pushes the anvil. The apparatus was used to measure the effect of pressure on T_c of Al with a Squid manometer to detect the change in the magnetic moment of the sample.

Mao and Bell (1979) have developed low temperature techniques which are widely used with DACs down to liquid He temperatures. Here the central hole or the gasket chamber in the gasket is filled with liquid or high pressure H₂/He and then the cell is sealed. Thereafter the pressure can be increased or the temperature lowered. Shaw and Nicol (1981) described a simple DAC for optical spectroscopy to pressures of 10 GPa at temperatures down to 2 K. The cryostat is provided with optical windows and pressure is changed from outside by a helium-driven piston acting on a pivoted clamp. Diatschenko and Chu (1981) have developed a cryogenic press fabricated from Be-Cu, which enables sealing of the desired gas in central hole (the specimen chamber) of the gasket of the DAC and pressurization from outside the liquid-He and cryostat through a screw threaded mechanism. The system is used for optical observations on the melting behaviour of H₂ between 20 K and 300 K. Liebenberg (1979) devised a very simple technique for filling the central hole (the specimen chamber) of gasket with Xe. Solid xenon is found to be hydrostatic upto 30 GPa pressure. Besson and Pinceaux (1979) have developed a high pressure gas loading technique for filling the specimen chamber of the gasket with He. In this, a high pressure bomb with DAC inside is pressurized to 0.2 GPa. This technique has been modified by Mills *et al* (1980) for filling He and D₂ in a Mao and Bell (1979) cell. Weinstein (1984) used a DAC for luminescence, transmission and Raman scattering measurements at low temperatures (down to 4 K). Silvera and Wijngaarden (1985) developed a DAC with a cryostat suitable for optical studies down to 1.1 K. Kobayashi (1985) described a DAC which allows optical studies at low temperatures and variable pressure to 26 GPa. In this system a bellows assembly has been designed to drive the DAC and the connected helium gas pressure source. The details of the instrumentation will be discussed in the following sections.

The pressure calibration in DAC, has been achieved by studying the shift of the R lines of ruby under pressure. The R lines of ruby are quite intense and the doublet R₁ and R₂ have the wavelengths 6927 and 6942 Å respectively at atmospheric pressure. Under pressure these shift to higher wavelengths and the shift is linear with pressure. Piermarini *et al* (1975) linked the ruby scale to NaCl through the Decker equation of state (Decker 1971) and showed that it is linear upto 19 GPa. They proposed that $P = 0.2746 \Delta\lambda$ where P is in GPa and $\Delta\lambda$ in Å. A recalibration was needed for this applications of the ruby manometer to low temperatures, since the value of dv/dP changes from $-0.757 \text{ cm}^{-1}/\text{kbar}$ at 293 K to $-0.73 \text{ cm}^{-1}/\text{kbar}$ at 166.8 K. Noack and Holzappel (1979) calibrated the ruby pressure scale at low temperatures by using the helium gas pressures upto 1.2 GPa.

In the subsequent sections the instrumental techniques specific to various physical measurements like mechanical, electrical, magnetic, optical and structural properties will be discussed.

3. Mechanical properties

A knowledge of the mechanical behaviour of materials at high pressures and low temperatures is in some sense a prerequisite for many other studies. For example the very construction of an apparatus at this combination of extremes of conditions depends upon this knowledge, as discussed in §1.2. Apart from such technical applications, one may want to study the lattice properties of materials, for which a

combination of high pressures and low temperatures reduces lattice vibrations and atomic diffusions to very low levels. The earlier research on the mechanical properties of materials at low temperature and high pressures has been reviewed by Swenson (1960) and Stewart (1962).

The PVT measurements have been historically a very important area of work, which continues to attract attention. Many experimental techniques have been developed for these studies (Stewart 1962; Stajdohar and Towle 1964; Van Itterbeek 1965; Fujii and Nagano 1971; Padaki *et al* 1979). In the simple PVT measurements the sample is contained in the cylinder and the load is applied by the piston directly on the material under investigation (Swenson 1960; Landau and Wurfinger 1980; Kortbeek *et al* 1986). In some cases like the measurements of gases or liquids, the material is condensed into the chamber volume. The pressure is inferred from the load on the piston after correcting for frictional losses. The volume change or compressibility is estimated from the observation of the piston displacements (Alymov *et al* 1972), a correction being required for the dimensional changes of the piston and cylinder under pressure. Phase transitions are also detected from the displacement of the piston as a function of pressure. An interesting recent study of this type is the investigation of the various forms of ice at high pressures and low temperatures, giving a complex phase diagram (Whalley 1986). In addition to the PVT measurements the temperature variation of the shear strength of solid argon has been studied with this apparatus by Stajdohar and Towle (1964) using an extrusion technique.

Volumetric measurements have also been performed in the diamond anvil cells. Wieldraaijer *et al* (1982) have measured the size of the central hole (sample chamber) of the gasket in a DAC at various pressures. The chamber contains the medium under study and the thickness of the sample is measured interferometrically. The pressure is calibrated with ruby fluorescence and so one can obtain PVT data upto 30 GPa or more down to low temperatures.

Apart from the volumetric and compressibility measurements, some experiments on ultrasonic velocity measurements at high pressures and low temperatures have also been done (Homan *et al* 1978; Padaki *et al* 1979; Hazen *et al* 1980; Cromer *et al* 1981; Schiferl *et al* 1981). Van Itterbeek and Van Dael (1958) studied the sound velocity upto 75 atmospheres in gases and in liquids in the temperature range between 1 K and 350 K. The various techniques, in particular the piston-cylinder apparatus used for the sound velocity measurements in dense fluids at high pressures and low temperatures, are reviewed by Van Dael and Van Itterbeek (1965). Homan *et al* (1978) developed a continuous pressure and temperature changing system in which the ratio of longitudinal to transverse acoustic velocity can be measured as a function pressure upto 15 GPa and temperature down to 40 K. The schematic diagram of the sample area configuration is shown in figure 2. The ultrasonic transducers on each anvil area are exposed to approximately the same temperature as the samples; however they are at ambient pressures. These transducers allow acoustic interferometric measurements to be made on the argon pressure medium using a technique described by Frankel *et al* (1977). The ratio of acoustic velocities can be used as a pressure calibration parameter itself (Homan *et al* 1978). Many other techniques are described for the measurement of ultrasonic velocities at high pressures and room temperatures, which may be applicable at low temperatures also (Litov and Anderson 1978; Fujisawa 1984; Hagelberg and Corsaro 1985).

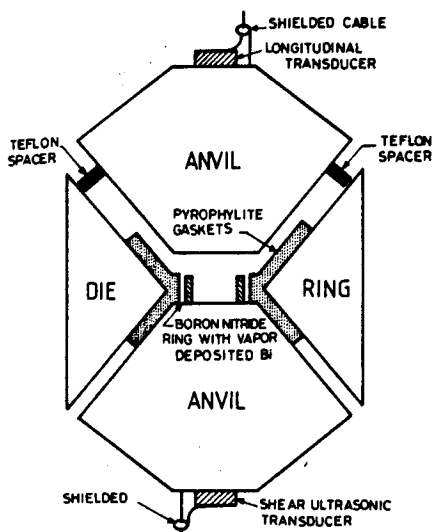


Figure 2. Schematic of the sample area in measuring ultrasonic velocities in an anvil apparatus.

Ultrasonic velocities can also be obtained from the Brillouin scattering experiments on the samples using the DAC technique, as discussed in the light scattering experiments.

The viscosity of fluids increases very rapidly at high pressures, by 6–7 orders of magnitude in some cases. An ingenious measurement of the coefficient of viscosity involves the Stokes fall of a sphere in a fluid, with the differences that the sphere is of a magnetic material and the accelerator force is not gravity but a magnetic field (Nishibata and Izuchi 1986). This method for measuring the viscosity and similar methods for measuring the friction can be easily adopted for h.p. work at low temperatures. Similarly self-diffusion data can be obtained from NMR measurements; measurements on alkanes at high pressure and low temperatures have been recently reported by Bachl and Ludemann (1986).

4. Thermal properties

The experimental methods of investigating the thermal properties of materials at atmospheric pressures can in principle be used at high pressures. There are however many difficulties and so modifications have to be made. In particular, one has a great difficulty in getting adiabatic environments for the sample at high pressures. So methods based on isothermal techniques have to be used (Lakshmikummar and Gopal 1981). For the investigation of plastic crystals in the low temperature region (100 to 300 K) and upto about 4 kbar pressure a new high pressure low temperature differential scanning calorimetry (DSC) microcalorimeter has been developed by Arntz (1980). The details of the measuring head are shown in figure 3. The heart of the device is a pair of identical cylindrical autoclaves, each of them closed by two Bridgman pistons made of Inconel 718, which are sealed by teflon. In the vessels (length 20 cm, o.d. 7 cm, i.d. 2 cm) made of a special austenitic nickel chromium steel (Amagnit 3974) for low temperature applications, the sample and reference holders are installed. The temperature is calibrated with cyclopentane and indium. Energy calibrations are based

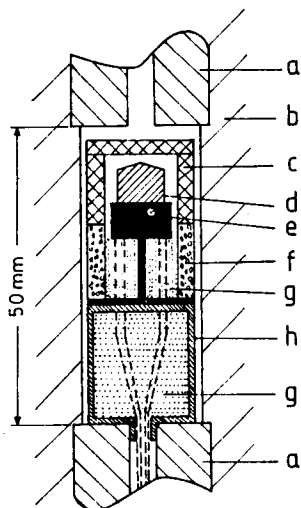


Figure 3. Head assembly of the high pressure differential scanning calorimeter.

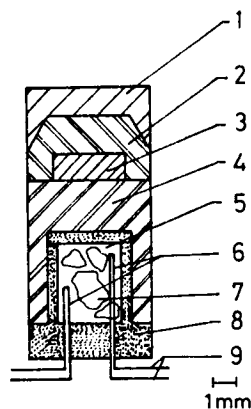


Figure 4. Cross-section of the calorimeter cell for use in a high pressure piston-cylinder apparatus.

on the transitions of cyclopentane, mercury and indium. Geijssel *et al* (1981) have developed a high pressure DSC apparatus working in the temperature range of 4 K to 1000 K and the pressure range upto 10 kbar. Solid ethane has been studied upto 12 kbar (Van der Putten *et al* 1986).

The specific heat measurements at high pressure and low temperatures, however, are rarely performed despite their valuable information on the type and distribution of excitations in the solid material as a function of the lattice parameters. The reason for this deficiency of calorimetric investigations is the technical difficulties arising from the high pressure conditions. In selecting the proper calorimetric method one has to make allowance for the fact that the sample cannot be thermally decoupled from its environment because of the pressure transmitting medium. Keeping these problems in mind, Eichler and Gey (1969) designed a high pressure-low temperature apparatus for specific heat measurements upto 35 kbar pressure and temperature down to liquid helium. The schematic diagram of the Eichler's pressure cell is shown in figure 4 (Eichler and Wittig 1968; Eichler and Gey 1969). Gallium was used as the embedding medium for the elements and the sample, because it is easily melted and moreover, is distinguished by a comparably high thermal diffusivity and a small specific heat at low temperatures. The pressure is determined from the superconducting transition temperature of a separately mounted indium sample (figure 4). Since it was separated from the calorimetric sample by layers of teflon and diamond powder some degree of pressure difference cannot be excluded (Andersson and Backstrom 1976; Ross *et al* 1977; Berton *et al* 1979; Siddiqui and Lucas 1982; Jin *et al* 1984; Pieper *et al* 1984).

The study of phase equilibria in gas mixtures is one of the most interesting phenomena in thermal properties (Bock and Wisniewski 1983; Balt *et al* 1983). Berman *et al* (1980) described a cell in which the solubility of solids in high pressure gases at low temperatures can be studied. The cell contains a magnetic stirrer, since mixing by diffusion is too slow at high pressure and low temperatures. The cell is

pressurized through a helium chamber. This apparatus is used for studying the pressure dependence of H_2 vapour concentration in He gas at low temperatures (down to 8 K). Street *et al* (1984) developed a device to determine the compositions of coexisting gas and liquid phases for binary mixtures of hydrogen with the following substances as the second component: nitrogen, carbon monoxide, argon, methane, ethylene, ethane and carbon dioxide (Calado and Street 1978). If the conventional equipment is used for the study of mixtures, the pressure range is limited to about 1.5 GPa. Recently Schouten *et al* (1979, 1986) developed a system consisting of a DAC with a high pressure vessel to match, which can be used for the phase behaviour of gaseous mixtures at pressures upto 10 GPa. This system is utilized for studying the gas-gas equilibrium in Ne-Xe, He- H_2 systems.

Ross *et al* (1977) developed a technique for measuring the thermal conductivity at high pressures (upto 2.4 GPa) and low temperatures (down to 120 K) by using a piston-cylinder apparatus. The pressure cell is used for measuring the thermal conductivity of different phases of ice and for studying alkali halide samples (Andersson *et al* 1986; Sigalas *et al* 1986).

5. Electrical properties

The high pressure studies on the electrical properties of the materials at low temperature, led to the discovery of many pressure-induced superconductors and other phenomena (Brandt and Ginzburg 1971; Bundy 1986b). Many questions are yet to be answered, for example, are there still other pressure-induced superconductors or can superconducting properties be destroyed by very high pressures. What about heavy

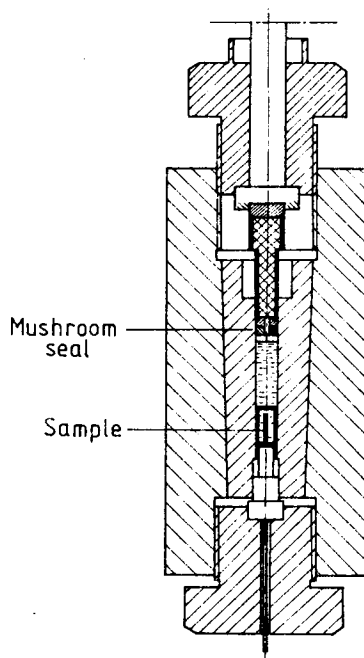


Figure 5. Beryllium-copper clamp cell for measuring electrical resistance and magneto-resistance at high pressures and low temperatures.

fermions, quasi one-dimensional materials, re-entrant superconductivity, organic superconductors and so on? (Smith and Chu 1967; Smith 1979; Wittig 1984; Chu *et al* 1986). In this section the techniques used in the study of the electrical resistivity, Hall effect, thermopower measurements at high pressures and low temperatures are briefly considered.

Figure 5 shows the schematic diagram of the clamp cell, developed by Itskevich (1964) to carry out low temperature experiments upto 1.8 GPa. The pressure production is closest to the method described by Vereshchagin *et al* (1958). All the parts of this cell, except the piston, the heel of the piston and the seals, are of Be-Cu. An oil-kerosene mixture is compressed in the cell by a piston equipped with a sealing device of the 'mushroom' type. The cell is cooled slowly after the pressure has been applied in the cell. The pressure calibration has been achieved by measuring the resistivity of manganin down to 20 K and with a tin manometer at 4 K (Itskevich *et al* 1966). Electrical resistivity measurements are carried out at 20 K and 0.1 GPa. Gaidukov and Itskevich (1964) have studied the pressure dependence on the Fermi surface of zinc. Itskevich's method has been used in various experiments, like optical experiments (Nefedova and Minin 1973; Shirokov *et al* 1973), thermal conductivities of metals (Itskevich and Kraidenov 1975) and electron spin resonance studies (Kozhukhar *et al* 1975). Fujii and Nagano (1971) have built a high pressure apparatus operating at liquid helium temperature for studying galvanomagnetic effects of materials at high pressures and low temperatures. The schematic diagram of the apparatus and the details of the piston-cylinder cell is shown in figures 6 and 7 respectively. It is a direct piston displacement type cell where the pressure and temperature can be changed simultaneously. The apparatus consists of a piston-cylinder cell made of Be-Cu alloys, compression and tension components made of stainless steel, and a high pressure oil pump. This apparatus has been used for studying magnetoresistance and Hall coefficient of Yb and Te upto 2.0 GPa at 4.2 K. A similar type of apparatus has been

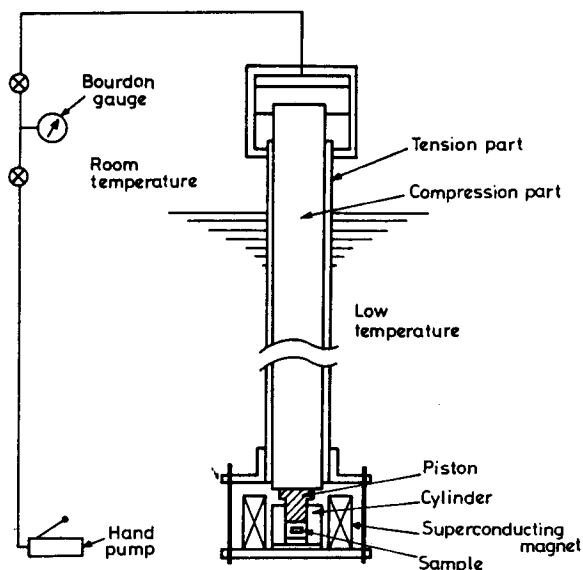


Figure 6. High pressure low temperature apparatus to study galvanomagnetic effects.

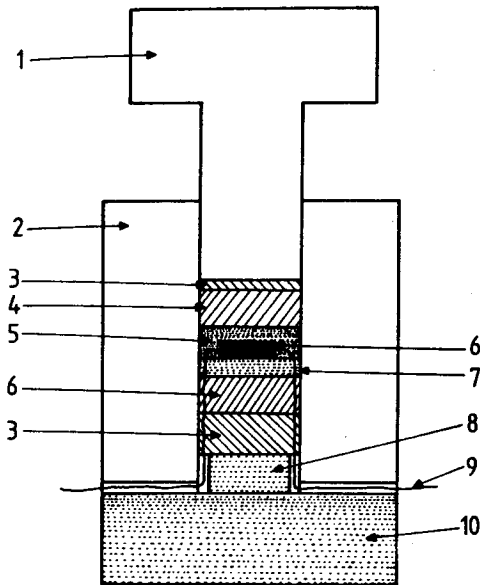


Figure 7. Details of the sample mounting for galvanomagnetic studies.

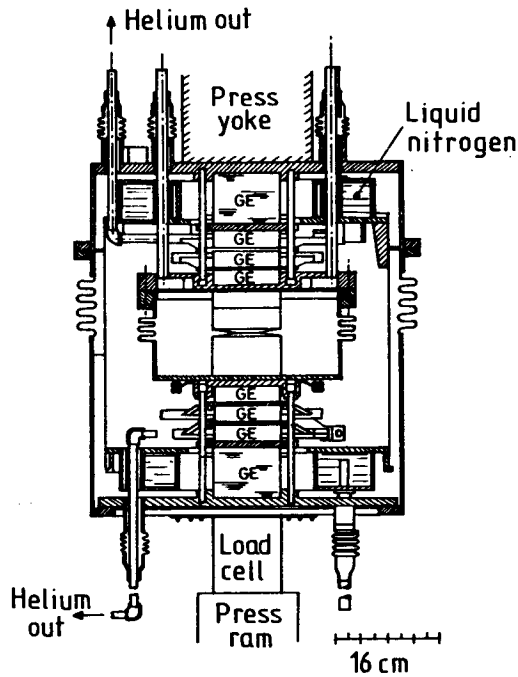


Figure 8. Low temperature high pressure cell with bellows for vacuum tight expansion joints.

developed for ultrasonic velocity measurements (Padaki *et al* 1979) and electrical resistivity measurements (Parthasarathy *et al* 1984) at high pressures and low temperatures. In the electrical resistivity measurements, the piston-cylinder cell has been replaced by the Bridgman anvil cell and the pressure range has been extended upto 8 GPa (Parthasarathy *et al* 1984).

Lyon *et al* (1967) fabricated an apparatus, which enables 10 GPa to be reached between 4 and 300 K (figure 8). The sample is compressed between two Bridgman anvils with the aid of a 270 ton press. The columns which transmit the compressing force to the cell consist of blocks of fibre glass epoxy. These are separated by molybdenum discs at the periphery of which heat exchangers are welded. These are in contact with helium vapour produced by the heat flow entering the experimental chamber (figure 8). The sample is compressed at room temperature and the cell is then cooled to low temperatures under constant load. This cell has been used for NMR experiments by Gossard *et al* (1970). A similar apparatus with a simplified construction has been built by Chaisse' *et al* (1970) to measure magnetic ordering temperatures upto 8 GPa between 10 and 300 K.

Vereshchagin *et al* (1969) developed an apparatus for superconductivity measurements upto 5.0 GPa (figure 9). The device consists of two pressure boosters, one of which is immersed in liquid helium. The first booster is always at room temperature, and can produce upto 1.0 GPa in oil. The oil under pressure flows along a stainless steel capillary through the sealed end of the Dewar flask into the low pressure chamber of the second booster, which consists of special steel vessels screwed together. The pressure intensification coefficient is about 40. This apparatus is exploited in the investigation of the pressure dependence of superconductivity of thallium (Vereshchagin *et al* 1969; Ilina and Itskevich 1970).

Figure 10 shows the apparatus developed by Wittig (1966) to study the pressure dependence on the superconducting of lead and tin upto 16 GPa. The sample is embedded in a steatite pressure-transmitting medium, which is surrounded by a pyrophyllite gasket. Fujii and Nagano (1972) have described a cell in which the anvils remain under compression by means of a system of two flanges and three bolts. Similar

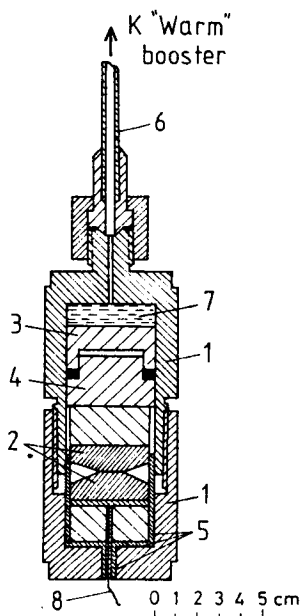


Figure 9. Low temperature pressure intensifier using anvil assemblies to study superconductivity.

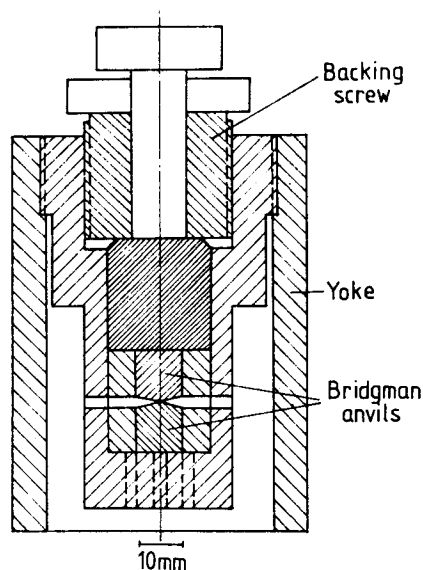


Figure 10. Clamp cell for use up to 100 kbar at low temperature, using a lock nut.

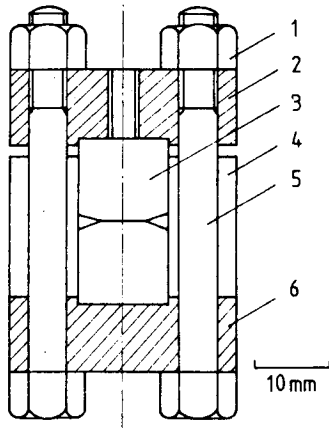


Figure 11. Clamp cell for use at low temperatures using a bolt arrangement.

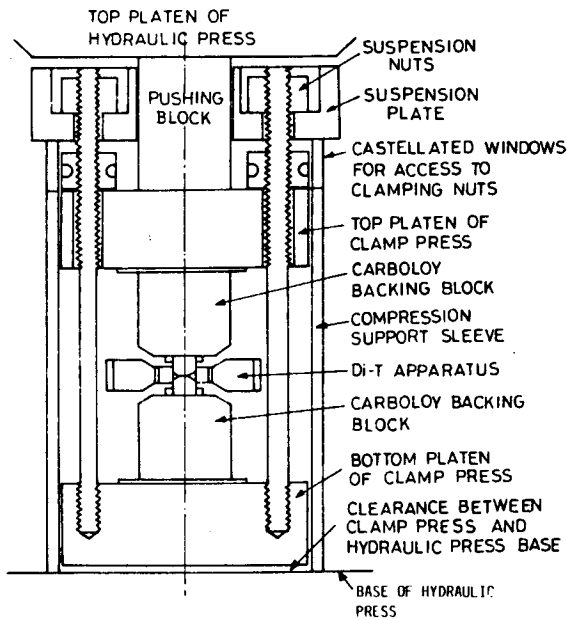


Figure 12. 50 GPa clamp-type anvil arrangement to study electrical resistivity at low temperatures.

clamp type cells have also been developed by Bandyopadhyay *et al* (1980). It is best to use this type of clamp cell for attaining temperatures lower than 100 mK, because of its small heat capacity and its small heat leakage during the experiment. A typical high pressure clamp cell for electrical resistance is shown in figure 11 (Fujii *et al* 1972; Bandyopadhyay *et al* 1980).

The above two techniques namely continuous pressure changing system and the clamp techniques are being utilized widely in the electrical resistivity measurements by many researchers with minor modifications to suit each experiment (Vereshchagin and Semechan 1961; Balchan and Drickamer 1961; Buckel and Gey 1963; Clark 1964; Itskevich 1964; Levy and Olsen 1965; Mcwane *et al* 1968; Pitt 1968; Smith *et al* 1969;

Pitt and Lees 1970; Wohlleben and Maple 1971; Smith 1972; Fujii *et al* 1974; Shimomura *et al* 1974, 1976; Kendall *et al* 1975; Homan 1975; Anzin *et al* 1976; Brandt *et al* 1976; Itskevich and Kraidenov 1978; Willer and Moser 1979; Kojima *et al* 1979; Itskevich *et al* 1979; Takemura *et al* 1979; Lories Susse 1980; Kawamura and Tachikawa 1980; Akahama *et al* 1986).

Electrical resistance measurement with DAC is one of the most challenging problems in the high pressure experimental science (Nelson and Ruoff 1979). Bundy and Dunn (1980a, b) have made extensive electrical resistivity measurements on several elements upto 50 GPa pressure at temperatures down to 2.7 K. The pressure apparatus is shown in figure 12. All the highly stressed parts, aside from the diamond and cemented tungsten carbide were of special stainless steels which are not subject to brittle fracture at cryogenic temperatures. The geometry and the combination of materials used were such that the thermal shrinkage during cool down from 300 K to 2.7 K was the same in the tension and compression parts of the system, thus keeping the loading of the pressure cell about constant. After the cell was loaded and clamped, the assembly was transferred into a large stainless steel dewar. Figure 13 shows the assembly hanging in the large dewar by thin-walled stainless steel tubes. One of the tubes was for the introduction of cryogenic liquid and the other for purging out the cryogenic fluid by applying gas pressure to the dewar.

Webb *et al* (1976) have developed a DAC with He³-He⁴ dilution refrigerator, which is used to measure the effect of pressure on the superconducting temperature of Al, with a Squid magnetometer to detect the change in the magnetic moment of the sample.

Sakai *et al* (1982) have described a four-lead arrangement for measuring electrical resistivity in DAC upto 25 GPa pressure and at temperature ranges down to 2 K. Thin Cu or Pb lead wires are used as electrical leads. Helium gas pressure was applied to generate the load. Pressure was calibrated using Bi, Pb, ZnS and GaP as fixed points

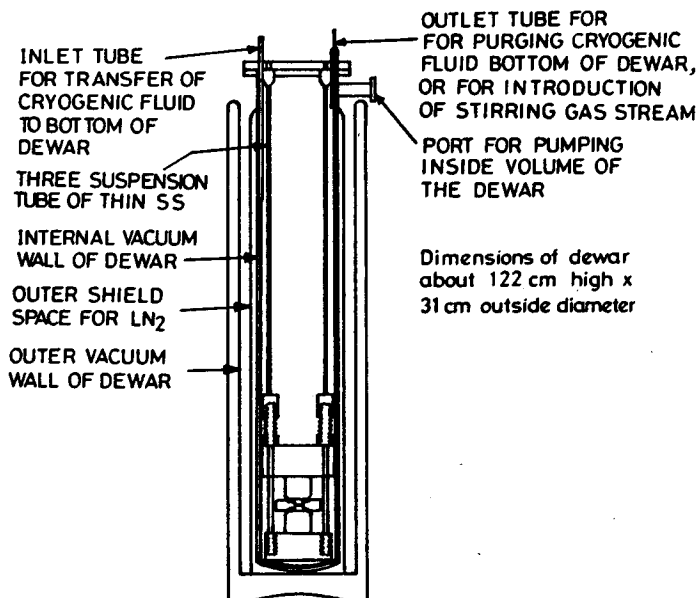


Figure 13. Pressurized clamp apparatus assembly hanging inside the large Dewar for cryogenic studies.

(Sakai *et al* 1982). Golopentia and Ruoff (1981) used spherically tipped diamonds with radii less than $1 \mu\text{m}$ to obtain 2 Mbars (= 200 GPa) pressure at 78 K.

5.1 Hall effect

Hall effect measurements under high pressure have been done by a few scientists. Benedek *et al* (1954) have reported Hall measurements on Ge upto 1 GPa hydrostatic pressure using Be-Cu vessel. Fujii and Nagano (1971) have developed an apparatus for studying Hall effect at high pressures and low temperatures, which was discussed in the previous section. Vyas *et al* (1973) developed an anvil technique for Hall measurements at low temperatures by circulating liquid nitrogen through copper coils encircling the anvils. The apparatus has been used for obtaining Hall data on GaAs upto 5 GPa pressure in the temperature range 120–300 K. Lifshitz and Maines (1979) have designed a high pressure (upto 4 GPa)-low temperature (down to 150 K) Hall apparatus, by adopting the teflon cell technique (Jayaraman *et al* 1967). Porowski *et al* (1977) designed a continuous pressure and temperature changing system in which Hall measurements and resistivity measurements can be made upto 2 GPa pressure at temperatures down to 4.2 K, with purely hydrostatic pressure environment (Kadri *et al* 1986; Zitouni *et al* 1986). In this apparatus liquid and solid helium are directly compressed in the piston-cylinder apparatus at 4.2 K (Jones *et al* 1975).

5.2 Dielectric constant

Wurflinger (1980) developed an excellent technique to measure the dielectric constant of molecular crystals and liquids in the temperature range between 210 K and 300 K upto a pressure of 0.3 GPa. The high pressure equipment is shown in figure 14. The inner (n) and outer (o) cylinders of the capacitor are separated by plastic spacers (p, l) and held together by a screw cap (k). The pressure is transmitted through the opening (i) on to the moving piston that consists of two parts (b, e) being separated by an indium sealing (d). A hollow space (c) between two parts works like 'Bridgman's unsupported

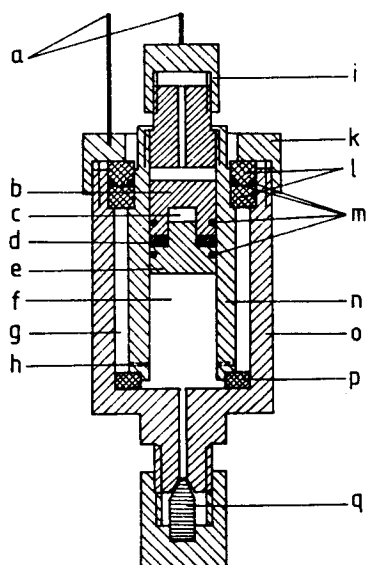


Figure 14. Dielectric cell for high pressure low temperature studies.

area'. By this method Wurfinger has achieved the sealing of the piston. Most of the electrode leads are guarded by the Bridgman piston that has two bores for the electrical feedthroughs. The piston and the vessel are connected with the grounded shield of the coaxial leads. With this arrangements lead capacities are avoided. Samara (1981) has made extensive studies on the pressure and temperature dependence of the dielectric constant of K_2SeO_4 by using a piston cylinder apparatus upto 1.4 GPa pressure and temperature down to 4 K. Samara (1984) found that K_2SeO_4 exhibit a λ -type anomaly in the variation of dielectric constant at the incommensurate-to-ferroelectric transition ($T_c = 93$ K). The transition temperature decreases rapidly with pressure and vanishes at a pressure above 0.72 GPa. The Peierl's transition in TaS_3 has been studied by Zhang *et al* (1981) under pressure, by thermopower measurements upto 1.9 GPa at temperatures down to 1.2 K. The Peierl's transition is first enhanced and then suppressed by pressure (Zhang *et al* 1981). Other dielectric cells for use at high pressures and low temperatures have been described by Thuillier *et al* (1986) and others.

5.3 Fermi surface studies

Hydrostatic pressures coupled with very low temperatures have proved to be very interesting in the study of the Fermi surface and electronic structure of metals (Brandt *et al* 1972; Schirber 1970, 1974, 1978, 1981; Gaidukov and Itskevich 1964; Itskevich 1984; Itskevich and Kashirskaya 1982). Figure 5 shows the Itskevich cell to carry out low temperature experiments upto 1.8 GPa. The main technique adopted for direct measurements of the Fermi surface is either high-field magnetoresistance or the attendant Shubnikov-de Haas oscillations. Stark and Windmuller (1968) developed a technique, which has the advantages of the field modulation deHaas-Van Alphen (DHvA) method. By this technique one could study the pressure effect on the Fermi surface of the metals without any electrical leads. DHvA effect, as well as other oscillation effects were measured in the Itskevich's cell by a modulation method in a magnetic field upto 80 kG (a superconducting solenoid with an inner diameter 6 cm). All the systems of modulation and detection coils were arranged within the cell.

6. Magnetic properties

Studies on magnetism under high pressures and low temperatures have yielded considerable information concerning the magnetic exchange interaction of electrons, magnetic ordering etc. For measuring magnetic properties of materials under high pressures, non-magnetic and hardened metals are required for the pressure vessel. Be-Cu alloy with Be concentration of about 1.82 wt% is the most popular material for construction (Patrick 1954; Adams and Davis 1958; Werner 1959; Bloch and Pauthenet 1962; Kouvel and Wilson 1961; Kondorski and Sedov 1960; Kawai and Sawaoka 1967; Fujii *et al* 1974; Alymov *et al* 1973; Fasol and Schilling 1978; Ribault and Benoit 1978; Schilling 1984).

Kawai and Sawaoka (1967) have developed a high pressure bomb capable of measuring weakly magnetic substances and anisotropy under hydrostatic pressure in a high magnetic field in the temperature range 4.2 K to 473 K. Kerosene and transformer oil in 1:1 ratio were used as the pressure-transmitting medium. The calibration has been done using a manganin gauge. Similar measurements were also carried out by

Svechkarev and Panfilov (1965). Apart from the magnetization experiments, techniques have been developed for measuring the Curie temperature as a function of hydrostatic pressure upto 2.5 GPa (Samara and Giardini 1965; Kaneko *et al* 1981; Kadomatsu *et al* 1982). Samara and Giardini (1965) developed a self-inductance method to find the Curie temperature and Kaneko *et al* (1981) determined the Curie temperature by the a.c. transformer method.

6.1 Magnetic susceptibility

Studies of the effect of pressure on the magnetic susceptibility help to understand some aspects of the structure of the energy spectrum of electrons in weakly magnetic metals and their alloys (Fujikawa *et al* 1980; Eiling *et al* 1981; Vining and Shelton 1984; Schilling 1984). Alymov *et al* (1973) have designed an apparatus, shown in figure 15. It consists of a press (1) with drive, motor (2), reduction gear (3), two dewars (4, 5) for liquid helium and nitrogen and the measuring arrangement; dynamometer (6), dilatometer (7), and coil (26) for registering the change in susceptibility. The press is connected with a vacuum packing to the top of the helium dewar by tube (8) which is firmly fixed to the casing. The sample (9) is kept in the high pressure chamber (10) and is compressed through the thrust block (11) by the advancing nut (12), which is set in motion by the electric motor (2), with a reduction gear (3) (or manually by a wheel (13)), through the

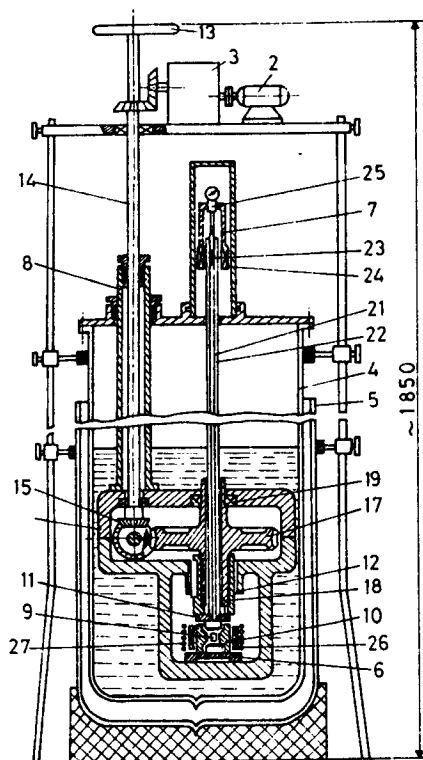


Figure 15. Measurement of magnetic susceptibility at high pressures and low temperatures.

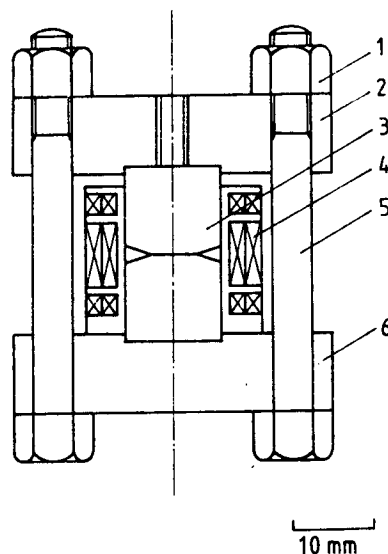


Figure 16. High pressure clamp arrangement for magnetic susceptibility measurements at very low temperatures.

tubular shaft (14), the pair of conical gears (15), worm (16), worm wheel (17) and screw (18). The axial load on the screw is taken up by the ball thrust bearing (19). Calibration at 4.2 K was carried out by measuring T_c of a Sn specimen in the chamber at various pressures. A superconducting or magnetic transition in the specimen is observed as a function of pressure with measuring coils (26).

Fujii *et al* (1974) have made an excellent high pressure clamp cell with dilution refrigerator for a.c. magnetic susceptibility measurements (figure 16). The primary and the secondary coils are both divided in three parts. The coils are wound with an insulated copper wire (0.08 mm diameter). The inner coil is the primary with 900 turns in the same direction. The outer coil is the secondary which is 2000 turns. The turn of the second middle part of the coil is reverse in its direction from the first (upper) and the third (lower) part and the induced voltages from each parts of the coil are compensated. The detection of the superconducting transition by the magnetic method need not require any electrical leads. The clamped high pressure cell is attached to the bottom of the mixing chamber of a $^3\text{He}/^4\text{He}$ dilution refrigerator and is cooled down to 30 mK. Webb *et al* (1976) have described an apparatus for the investigation of the magnetic properties up to 10 GPa at temperatures down to 30 mK. This apparatus incorporates a DAC, that is cooled by a $^3\text{He}-^4\text{He}$ dilution refrigerator (figure 17). Changes in the magnetic moment of the sample (0.1 mm in diameter, 0.2 mm high) were detected with a SQUID magnetometer. Ribault and Benoit (1978) developed a high pressure Be-Cu cell for nuclear orientation experiments upto 2 GPa pressure and temperatures down to 8 mK.

Paureau (1977) discussed an apparatus for magnetic measurements under high pressure upto 2 GPa at a field of 10 T in the temperature range 2 and 300 K (figure 18). This apparatus can be equipped with either a helium pressure system (upto 1 GPa) or a piston-cylinder cell for pressures more than 1 GPa. The cell is connected to an outside

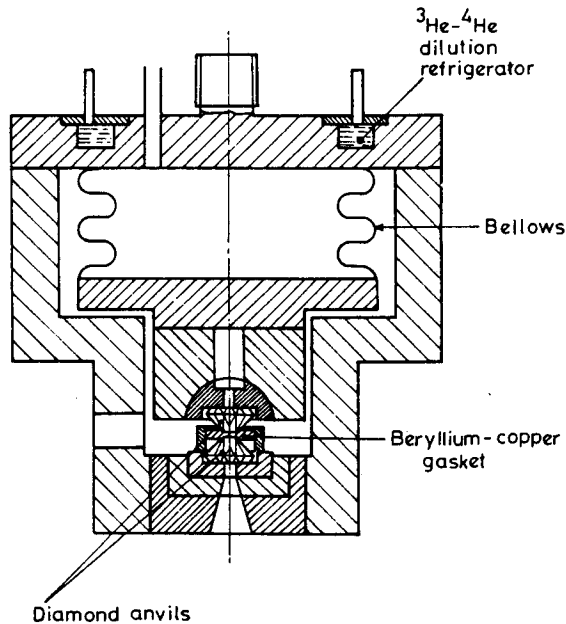


Figure 17. Diamond anvil cell for magnetic measurements in the milli-kelvin region.

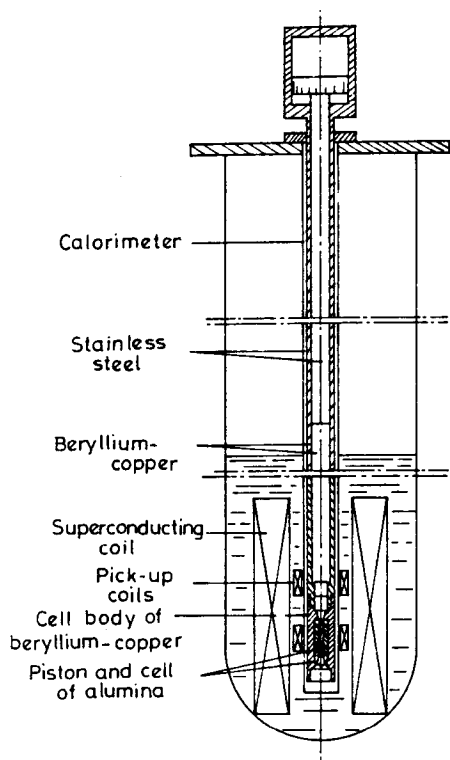


Figure 18. Magnetic balance for use at high pressures and low temperatures.

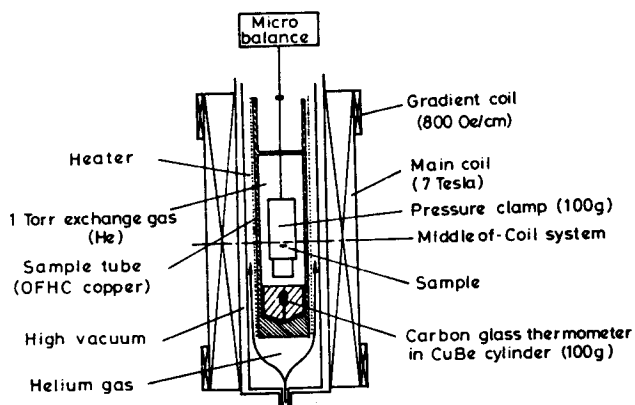


Figure 19. Faraday magnetometer for low temperature high pressure studies.

jack. The components of the high pressure cell are made from Be-Cu alloy except for the pistons and the core of the cell, which are made of high strength alumina. Lead is used as a compressing medium and manometer. Fasol and Schilling (1978) developed a hydrostatic pressure cell up to 9 GPa for precise magnetic measurements at temperatures between 1 K and 300 K. Eiling *et al* (1981) have measured the magnetic susceptibility and the upper critical field in a Faraday balance system, which is shown in figure 19. In this apparatus a small high pressure clamp (1.8 cm dia, 5 cm length,

100 g total weight) is in a magnetic field of constant $H(dH/dZ)$ value i.e. a constant force over the volume of the clamp. The balance system spans the temperature range 2.5–300 K with 7 T maximum field at hydrostatic pressures up to 1.5 GPa. The pressure is calibrated with a Pb manometer. The apparatus is extensively used for the investigation of the superconductivity of lanthanum chalcogenides (Eiling *et al* 1981). Some workers have used the piston-cylinder device for the susceptibility studies at high pressures and low temperatures, though the pressure range is limited to 2 GPa (Menyuk *et al* 1969; Wohlleben *et al* 1971; Guertin and Foner 1974; Hardebush *et al* 1980; Ido and Satosh 1982; Usha 1984).

Alekseevskii *et al* (1983) have studied the effect of pressure on the critical temperature of Chevrel phases with magnetic impurities at 2.0 GPa over a temperature range down to 0.1 K. They used Bridgman anvils made of yttrium-aluminum garnet single crystals ($\text{Er}_x\text{Y}_{3-x}\text{Al}_5\text{O}_{12}$; $x \approx 1.5$). High pressures at extremely low temperatures (0.1 K) were obtained by compressing a sample in yttrium-aluminium garnet anvils and then adiabatically demagnetizing the compressed system (Alekseevskii *et al* 1985). The temperatures below 1 K were determined from the magnetic susceptibility measurements, using the Curie law. The adiabatic demagnetization from a temperature of 1.5 K and a field of 12 kOe, yielded a low temperature of 0.1 K.

7. High pressure-low temperature cells for optical studies

The high pressure optical cell with alkali halide as the pressure-transmitting medium was developed by Drickamer *et al* (1957) as the first major tool for optical studies. Later Sherman (1966) developed a variable temperature, high pressure optical cell which could be used at temperatures down to 80 K and pressures upto 5 GPa. The bulk of the cell is constructed from EN 26 steel rods. Larger windows than those used by Drickamer *et al* (1957), improved the light throughout, but it was found necessary to use sapphires as end seals since there was considerable extrusion of NaCl above 1.5 GPa. Sapphire windows have been used in the ellipsometric studies of solid helium (Franck *et al* 1986). Sapphires are also transparent up to 5 microns but other materials may be used to widen the spectral range. Lewis and Sherman (1974) developed a new liquid helium cell for high pressure optical studies. In construction, the cell design is similar to 80 K cell of Sherman (1966). The helium cell is much smaller than the 80 K cell. Moreover, the helium cell is constructed with tungsten carbide piston. About 5 litres of liquid helium are required to bring the cryostat and high pressure cell down from 77 K to 4.2 K. A further 3 litres almost fills the cryostat which then maintains its terminal temperature for 10 to 12 hr. The cell has been used for studying the absorption spectra of $\text{CsCl}/\text{NH}_4^+$ crystals at different pressures and temperatures.

Shchanov and Subbotin (1974) designed a high pressure cell with three optical windows so that absorption and emission spectra can be studied as well as reflection, luminescence and Raman spectra, up to 5 GPa pressure at temperatures ranging between 80 and 300 K. The chamber is placed for cooling in a cryostat consisting of a metal jacket covered with foam plastic and filled with liquid nitrogen. Anzin *et al* (1976) described a continuous pressure and temperature changing system for optical investigations up to 1.5 GPa in the temperature range 15–300 K. There are other high pressure-low temperature optical cells available, with essentially the same design (Medvedev *et al* 1978; Yamada and Schmidt 1978; Voloshin and Kasyanov 1980, 1982;

Dawson and Offen 1980; Dahan *et al* 1982; Daniels 1983; Ackermann *et al* 1985; Watson and Daniels 1986; Klug *et al* 1986).

Weinstein (1984) developed a variable pressure (0–30 GPa) and temperature (4–300 K) cryostat for luminescence studies. The cryostat is shown in figure 20. A Be-Cu DAC consisting of a piston in cylinder arrangement with diamond mounts threads into the outer tension sustaining tube. The inner tube provides compression to the DAC piston when activated by the room temperature hydraulic cylinder at the top. Optical access is through the bottom cryostat window and bottom diamond, or through the internal microscopic arrangement and the top diamond. The cryostat insert sits in a He-gas flow variable temperature optical dewar. The entire arrangement can be evacuated or purged which is necessary during loading and cooling. The pressure is calibrated by a ruby manometer.

The DAC for cryogenic temperature with optical measurement systems have been described independently by Shaw and Nicol (1981), Silvera and Wijngaarden (1985), Kobayashi (1985), Kawamura *et al* (1985) and Kourouklis *et al* (1986). The Be-Cu DAC and cryostat suitable for optical studies from 1.1 K to 300 K is shown in figures 21 and 22 respectively (Silvera and Wijngaarden 1985). Since cryostats are most easily built in a long, cylindrical shape, the cell assumed the form shown in figure 21. A cross-sectional view of the heart of the DAC is shown in figure 21(a). One diamond was mounted on a cylindrical platform 1 which has an x-y translation adjustment to allow for positioning of the diamonds opposite to each other. This platform was mounted on part 2 which screws into the main block and allows easy access to the diamond for preparation of the gasket, etc. The other diamond was mounted on a half sphere (part 3) which allows for 2° of rotation to align the diamond faces parallel to each other. This was mounted in part 4, a precision ground cylinder which is translated horizontally by a force applied to part 5. The means of applying the force is shown in figure 21(b). The screw at the top was

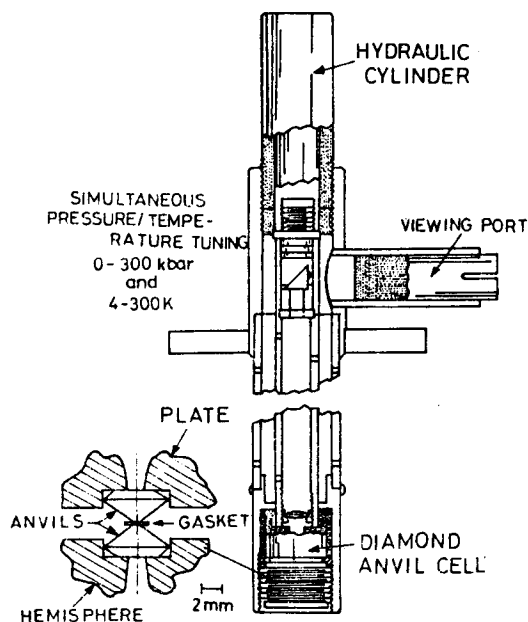


Figure 20. Cryostat for luminescence studies at high pressures using a DAC.

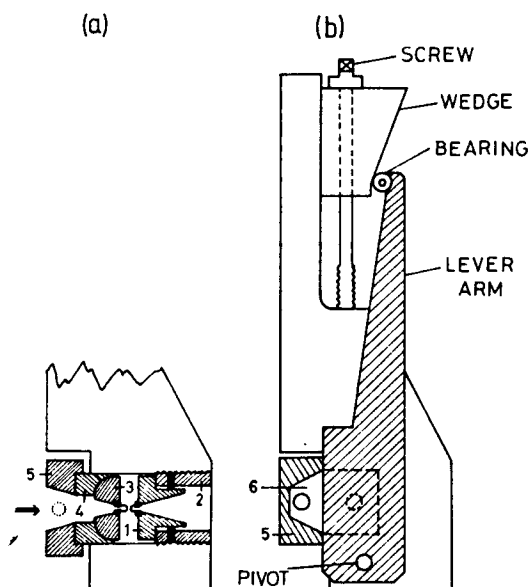


Figure 21. Details of the beryllium-copper DAC suitable for low temperature use.

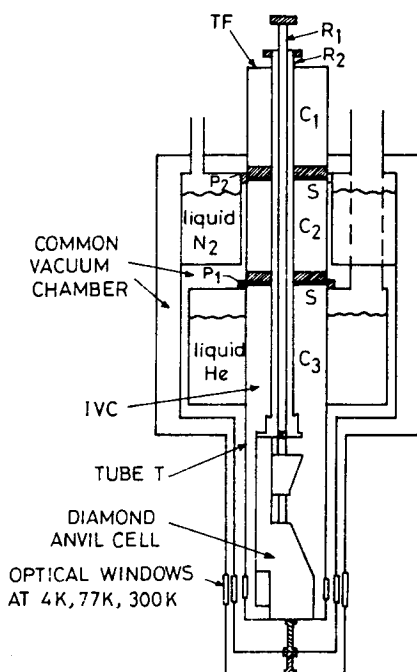


Figure 22. Liquid helium Dewar containing the DAC and the support structure.

turned to drive the wedge down. Figure 22 shows the stainless steel liquid helium cryostat with DAC mounted in the inner cylinder. The cell has been used to study the phase transitions in molecular H_2 and D_2 (Silvera and Wijngaarden 1981; Wijngaarden and Silvera 1980; Van Straaten *et al* 1982).

8. X-ray diffractometry at high pressure and low temperatures

The Bridgman's opposed anvil systems have been extensively used in high pressure x-ray diffraction studies over the last 20 years (Jamieson and Lawson 1962). Syassen *et al* (1971) developed a high pressure cell for x-ray diffraction, Mössbauer and nuclear gamma angular correlation studies on solids at temperatures between 4.2 and 350 K and pressures up to 18 GPa. Morosin and Schirber (1974) developed a Be-Cu cell capable of going to high pressure ~ 0.4 GPa, over the temperature range 80–300 K. This cell is used for single crystal x-ray studies. Skelton *et al* (1977) developed a variable pressure DAC for operation at temperatures continuously variable from 300 K down to 2 K and controllable within 10 mK. Figure 23 shows the cross-sectional view of Skelton's cell. The diamond anvils are seated on sintered tungsten carbide pellets and the pressure cavity is formed by a 0.2 mm diameter hole drilled in a metal gasket, contained between the diamond anvils. A $\pm 30^\circ$ aperture is provided on the exit side of the cell. The pressure cell is connected to the temperature control block of a refrigerator through an indium gasket; this interfaces to a remote He storage dewar. The refrigerator system is equipped with Pt and Ge thermal sensors and temperatures between ambient and 4.2 K can be set and roughly controlled by adjusting the rate of He flow through the system via a micrometer needle valve. The rate of consumption of liquid He at 5 K is less than 1 litre/hr. Pressures were calibrated through sodium chloride. The mixture of methanol-ethanol-glycerine was used as the pressure-transmitting medium. This apparatus was used to study the low temperature phase diagram of bismuth (Skelton *et al* 1977).

Syassen and Holzapfel (1978a,b) devised an excellent high pressure low temperature x-ray powder diffractometer. The system consists of a Bridgman anvil type high pressure device with either tungsten carbide or boron carbide anvils, a liquid He cryostat and x-ray diffractometer operating in Debye-Scherrer geometry. Figure 24 shows the schematic drawing of the Holzapfel's cell. The top anvil is made of tungsten carbide and the bottom anvil is made of boron carbide. B_4C is sufficiently transparent

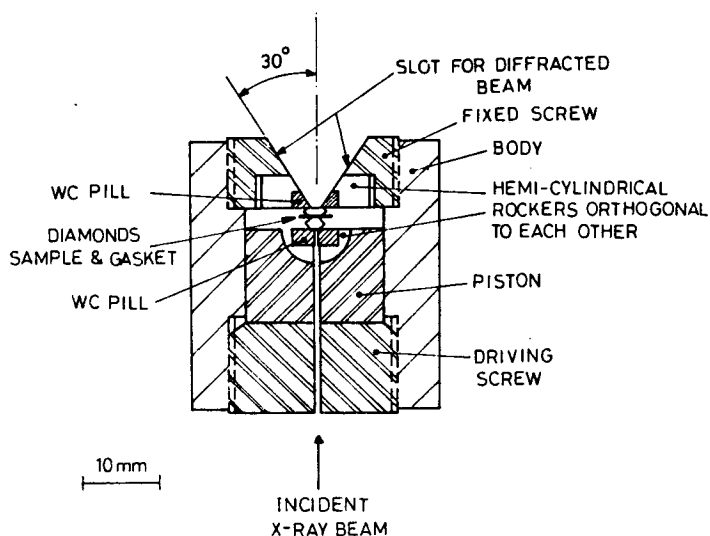


Figure 23. Diamond anvil cell with tungsten carbide sealing suitable for x-ray studies.

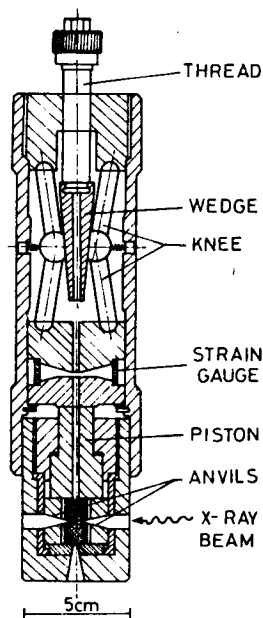


Figure 24. Anvil apparatus for x-ray studies.

to hard x-rays. For MoK_α radiation, the absorption length is about 8 mm. Both anvils are prestressed in the usual manner by supporting rings. The sample fills a small hole in a gasket on the tip of the B_4C anvil. By squeezing the two anvils together, the metal disk on the top of the hole deforms. A pressure gradient develops across the metal disk with maximum pressure in the centre just above the sample. The gasket then starts to flow into the sample region and thereby acts like a piston pressurizing the sample. X-rays pass through the B_4C anvil just below the metal disk.

A pair of coupled screws with opposite turning direction drives a wedge between two knees. The knees straighten and a maximum force of up to 15 tons can be exerted on the anvils. The advantages of this design over other designs are that (i) friction between the moving parts is reduced considerably and (ii) the overall torque on the apparatus during pressure change is zero. Therefore the Holzapfel's device is easier to handle inside a cryostat at low temperatures (Noack and Holzapfel 1978; Holzapfel 1984). Another useful device for single crystal work has been developed by Keller and Holzapfel (1977). The special shape of Be supports for the diamonds reduces the problem of x-ray absorption corrections in Be to a constant factor. The steel backings have wide conical apertures for the transmission of the diffracted x-rays over a wide angle. The device is capable of generating pressures of 10 GPa. Buras *et al* (1977) were the first to combine DAC with synchrotron radiation sources for high pressure x-ray diffraction studies and more recently Skelton *et al* (1984) and Spain *et al* (1981) have used DAC operated at cryogenic temperatures with synchrotron radiation. In order to provide pressure control at cryogenic temperatures, Skelton *et al* (1984) coupled the DAC to a dilution refrigerator with a bellows attachment capable of loading the piston of the DAC through a lever arrangement. The apparatus has been used to study the two critical points in the P-T diagram of number of Ce-rich Ce-rare earth-La alloys. A few other arrangements are described in the literature, which are essentially the same in principle as one of the above techniques (Alt and Kalus 1982; Spain 1984; Mouden *et al* 1980; Merrill and Bassett 1974).

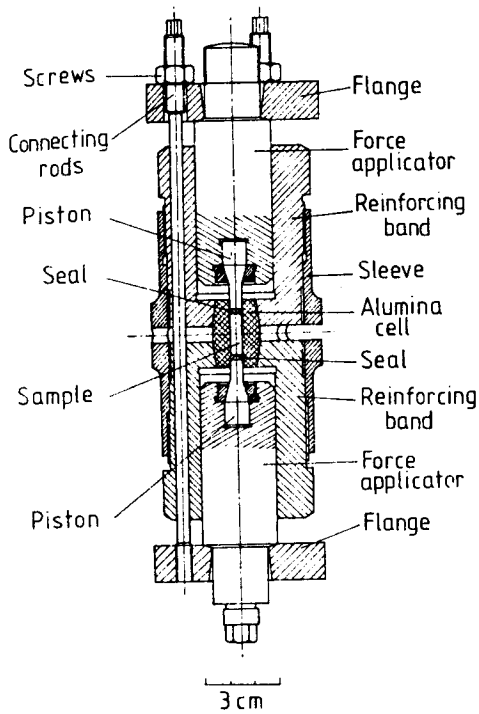


Figure 25. High pressure cell for neutron diffraction studies from 4 K to 300 K.

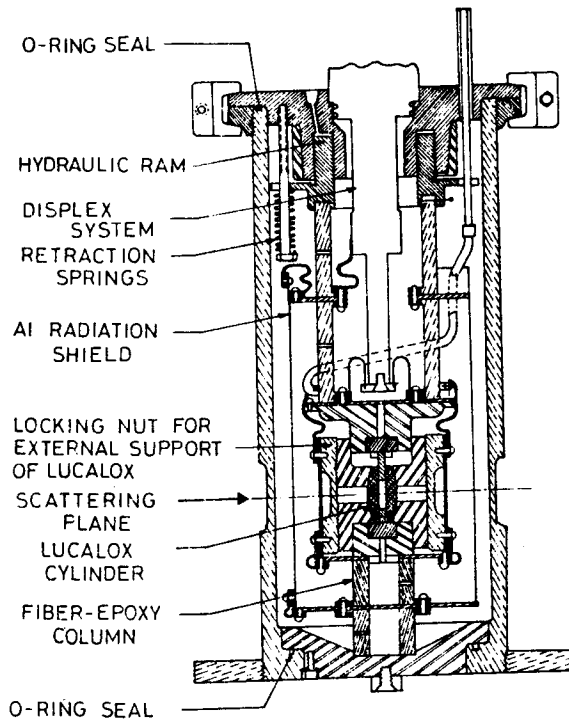


Figure 26. Neutron scattering high pressure cryostat with closed cycle refrigerators.

9. Neutron scattering at high pressures and low temperatures

The first inelastic neutron scattering experiments in the pressure range of 1 GPa were done in 1975. The cell design for high pressure neutron scattering depends on various parameters, such as the sample dimensions, sample absorption and temperature range. The construction materials should have sufficiently good transparency for neutrons. They are mainly aluminum alloys (Al-Zn-Mg-Cu), copper alloys (Cu-Be), maraging steels (Fe-Ni-Co-Mo) or alumina (Al_2O_3). For pressure-transmitting media, hydrogen compounds are not used due to their large incoherent scattering. The most common pressure-transmitting media are helium, C_6F_{12} fluorinert and deuterated ethanolmethanol mixture (Bloch *et al* 1976; Jansen and Will 1980; Vindryaevskii *et al* 1980; Mizuki and Endoh 1981; Kalus and Alt 1981; Kamigaki *et al* 1983; Walter 1984; McWhan 1984; Wu and Whalley 1985).

Standard cryostats are made of aluminium, which is transparent to neutrons. High pressure cells can be connected to a high pressure generator by means of a high pressure tubing. Clamped systems, with sufficiently small dimensions, allow conventional neutron cryostats to be used, as available in most reactors, without major consideration for low temperature problems (Bloch *et al* 1976). Another technique is to transmit the applied load from a hydraulic ram at room temperature to the pressure cell at low temperatures via insulating systems (McWhan 1979).

Figure 25 shows the Bloch's cell (Bloch *et al* 1976), which has been used from 4 K to 300 K and working pressures up to 0.4 GPa. The sample has a volume up to 5 cm^3 . A shielding allows for safety in the reactor context. These cells have been used for 2-axes elastic scattering, 3-axes inelastic scattering as well as 4-circles elastic scattering experiments.

McWhan (1979) described a low temperature press, where a closed-cycle helium refrigerator is used to transmit the applied load from the hydraulic ram to the pressure cell via hollow fiber glass epoxy columns. The closed-cycle helium refrigerator has two cooling stations which are attached through flexible links to outer and inner radiation shields (figure 26). Temperatures of 20 K and pressures of 2 GPa have been achieved with this apparatus.

10. Raman spectroscopy at high pressure and low temperatures

The principal problem of high pressure Raman spectroscopy is to lead light into and out of a high pressure cell. In the scattering experiment, the incident light is monochromatic, and the intensity of the scattered light is measured as a function of frequency. The first Raman studies with DAC were reported by Brasch *et al* (1968) and Postmus *et al* (1968), employing forward scattering geometry. Adams *et al* (1973) found that good Raman spectra are obtainable with back scattering geometry. Many investigations have been performed on Raman effect in various materials at high pressure and room temperature (Jayaraman 1983). Only a few studies have been attempted at low temperatures (Morosin and Schirber 1974; Hawke *et al* 1974; Adams *et al* 1976; Kojima *et al* 1979; Jodl and Holzapfel 1979; Abdullah and Sherman 1980; Hirsh and Holzapfel 1981; Mazzinghi and Zoppi 1983; Hanfland and Syassen 1985; Wong 1985). Hirsch and Holzapfel (1981) have modified the Holzapfel' cell by providing a sapphire backing for the diamond to increase the angular aperture for the

scattered light. The sapphire block is about 10 mm in diameter, and 10 mm high and is surrounded by a slightly tapered sleeve. A simple cryostat with optical windows can be used for low temperature studies down to 77 K (Hirsch and Holzapfel 1981). Sharma *et al* (1980) have studied Raman spectra of H₂ up to 62.3 GPa using a DAC. Medina (1980) developed an optical cell for far-infrared spectroscopy up to 1.0 GPa pressure in the temperature range 10 K to 300 K. Kojima *et al* (1979) measured the Raman scattering at high pressures and low temperatures by using a DAC dipped in a liquid He cryostat combined with a double monochromator and Ar ion laser. This apparatus has been proven to be capable of measuring the polarized Raman spectra up to 5.0 GPa pressure and the unpolarized Raman spectra up to 20 GPa pressure.

11. NMR and ESR at high pressure and low temperatures

The nuclear magnetic resonance (NMR) studies at high pressures are of great use in understanding the magnetic interactions in solids at a microscopic level. Though many articles discuss the NMR techniques at high pressures, only a few of them concentrate at low temperatures (Benedek 1963; Hauer *et al* 1980; Jonas 1980; Jonas *et al* 1981; Kiselnik 1983; Trokiner *et al* 1984). In high pressure-low temperature NMR studies the piston-cylinder apparatus made of Be-Cu alloy is commonly used (Cvec and Srinivasan 1978; Ramanathan and Srinivasan 1978; Sinha and Srinivasan 1983; Trokiner *et al* 1986). Sinha and Srinivasan (1983) have developed a clamp-type high pressure cell up to 1.0 GPa for NMR and EPR studies down to 77 K. Only a change of the bottom plug is required for a switch from a NMR to EPR experiment.

The mixture of *n*-pentane and isopentane in 1:1 ratio is used as the pressure-transmitting medium. The high pressure cell is calibrated at low temperatures by using a manganin pressure gauge. Huber *et al* (1984) developed a NMR probe head for high pressure studies up to 0.7 GPa. Helium gas is used as the pressure-transmitting medium. The apparatus is used to study the phase diagram of RbAg₄I₅ in the temperature range 77–300 K.

Van der Putten *et al* (1985) have devised a liquid helium cryostat containing a high pressure NMR probe, suitable for 1.5 GPa pressure in the temperature range from 2 to 100 K. The pressure cell consists of a two-part Be-Cu pressure vessel. The bottom part consists of a cylinder with an o.d. of 55 mm and length of 120 mm. The top part is fixed to it by means of a Be-Cu nut. The Be-Cu electrical feedthrough of the rf voltage to the NMR coil is mounted in the semispherical top part which is shown in figure 27 (Goedegebure *et al* 1977). The feedthrough, which meets the requirements of sealing at liquid He temperature and high pressure, has been developed by Schouten *et al* (1979). The top part of the pressure vessel contains a channel connected to the high-pressure capillary, used for filling and pressurizing the sample volume. This low temperature, high pressure probe was used in a series of NMR investigations of the properties of solid methane.

Stankowski *et al* (1976) performed EPR measurements up to 600 MPa in the temperature range 80 K to 400 K. The apparatus consisted of a cylindrical corundum resonator with TE₁₁₂ type wave directly coupled to the wave guide by means of a matching corundum wedge. The pressure chamber, in which the resonator with two plugs was placed, was made of non-magnetic beryllium bronze. Prokhorov *et al* (1983) developed an ESR cell for pressures up to 1 GPa at temperatures 1.5 to 4.2 K. Sakai

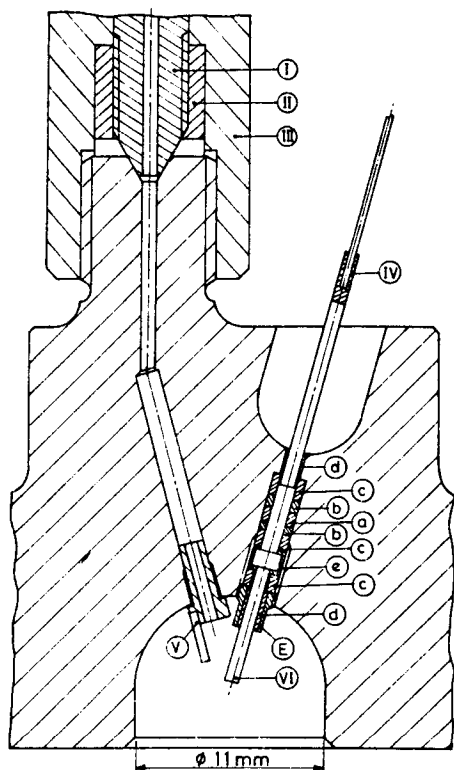


Figure 27. Electrical RF feedthroughs for high pressure NMR studies.

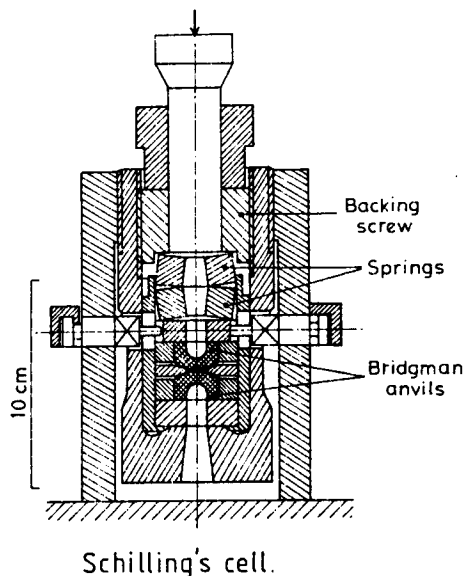


Figure 28. High pressure cell for Mössbauer studies at low temperatures.

and Pfler (1985) have developed a high pressure DAC for EPR studies. The technique for studying biomolecules at high pressure by EPR has been developed by Cannistarto (1984).

12. Mössbauer spectroscopy at high pressures and low temperatures

The effect of high pressure on Mössbauer spectroscopy of solids has been reviewed by many scientists (Holzapfel 1970, 1975, 1978; Drickamer *et al* 1965, 1969, 1970). High pressure Mössbauer studies at low temperatures are generally performed in clamp type cells (Christoe and Drickamer 1969; Syassen *et al* 1971; Schilling *et al* 1974; Liu and Ingalls 1978; Nikolaev and Potapov 1981).

Figure 28 shows the high pressure clamp cell developed by Schilling *et al* (1974) for Mössbauer studies up to 10 GPa pressures at temperatures down to 4.2 K. The major parts of the apparatus are made of Be-Cu alloy. The pressure on the sample was calibrated with a lead manometer. In the Mössbauer studies pressures in excess of 8 GPa were maintained at 4.2 K for periods of one week or longer (Bartunik *et al* 1970). Whitmore *et al* (1982) developed a ruby fluorescence system used for both Mössbauer and x-ray absorption spectroscopy with DAC at cryogenic temperatures.

13. Conclusions

An attempt has been made in reviewing the high pressure and low temperature techniques. Much progress has been made in this field after the introduction of the diamond anvil cell, which can produce 2 to 3 Mbar pressures at temperature down to few milli-Kelvin. A wide variety of the experimental techniques are available only for studying the transport and magnetic properties at high pressure and low temperatures. Spectroscopic measurements at high pressure and low temperature have been achieved in good measure only after the introduction of DAC in high pressure research. Though the piston-cylinder technique is the older one, limited in pressure range, this technique is still useful for NMR and ESR studies.

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