A tetrahedral anvil apparatus for optical studies under high hydrostatic pressures

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Abstract A method of modifying a tetrahedral anvil apparatus to allow optical experiments to be performed under high pressures and at low temperatures is described. Solid samples with dimensions of 2 or 3 mm can be studied within the following ranges: 0–50 kbar, 100–300 K, 2000–8000 Å. The system is designed so that at least two pressure calibration points can be obtained during each experiment. A method of pressure calibration at low temperatures is described. Such pressure calibration checks are necessary because the pressure–load curves vary markedly with temperature and tetrahedron design. The apparatus has been used to measure the pressure dependence of the energies of zero-phonon absorption lines in diamond.

1 Apparatus

The tetrahedral anvil equipment, as developed by The National Physical Laboratory and described by Bradley (1969), is used as the basis for an optical high pressure apparatus. Schematic sections through the apparatus are shown in figure 1. The anvils labelled 1, 2, 3 and 4 are arranged tetrahedrally in a steel cone. Anvils 1 and 3 have stepped holes which run concentrically along the axes of the anvils, and emerge as 3·25 mm diameter holes at the centroid of the triangular anvil faces which are made of tungsten carbide. The holes are 6·35 mm diameter through the steel backing blocks. The holes in the anvils may be aligned by eye with the 9·53 mm diameter holes in the steel cone. An oversize pyrophyllite tetrahedron (side length 28·6 mm) fits into the tetrahedral space between the four anvil faces. When a load is applied, pyrophyllite is forced between the anvils to form a gasket.

2 Design of the pyrophyllite tetrahedron

Holes of 6·35 mm diameter, passing through the centroid of each triangular face, are drilled perpendicularly to the respective faces so that they meet at the centre of the tetrahedron. Molten bismuth is poured into the resulting void and allowed to solidify. Fresh holes of diameter 5·00 mm are then drilled to leave the original holes lined with a thin layer of bismuth. Two of these holes are opened up again for the insertion of the optical windows, the outer optical surfaces of which are arranged to be just proud of the surface of the tetrahedron. The remaining space in the system is filled with optically clear cylindrical pellets of KCl, KBr or NaCl, the precise arrangement depending upon the nature of a particular experiment. The sample under investigation is usually positioned at the centre of the tetrahedron and is surrounded by a finely powdered dry alkali halide.

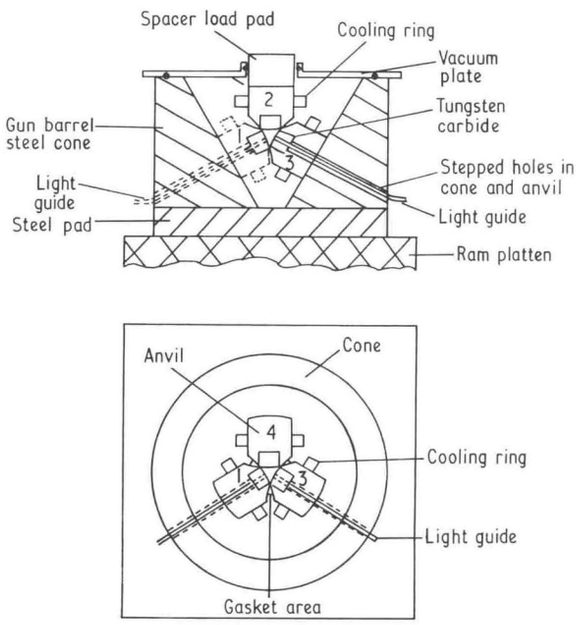

Figure 1 Schematic plan and section of a tetrahedral anvil apparatus used for optical studies

Two sorts of windows have been used: (i) synthetic single crystal sapphire cylinders of diameter 6·35 mm and length 3·18 mm, with the *c* axis parallel to the cylinder axis; (ii) diamonds in the form of polished rectangular blocks of dimensions 5 mm × 5 mm × 2 mm. The window and anvil faces that are in contact must be polished flat to within 5×10^{-5} cm. This reduces the risk of cracks developing from high local strains associated with point pressure contacts. The flatness tolerance also allows the 'ringing' together of the windows and anvil, thereby preventing pyrophyllite being forced between the window and anvil, which according to Poulter (1932) induces window breakage. The windows are positioned to cover symmetrically the 3·18 mm diameter holes in the anvil faces. In this arrangement the windows are subject to an almost uniform compressive force on all sides except that in contact with the anvil. The hydrostatic component of this force helps to inhibit crack formation and propagation.

Two examples of the use of the above system are illustrated in figure 2. In order to direct the light between the entrance and exit windows, the bismuth lining is polished, and aluminized Melinex discs are positioned to prevent light from entering the nonlight path arms of the system. For the duration of an experiment, and for half an hour before the load is applied, the cone is evacuated, thus helping to remove water from the hygroscopic halide powder, and aiding the sintering of the halide powder into a clear polycrystal on applications of the load.

In order to carry out optical measurements at low temperatures, cold dry air is passed through the anvil cooling rings

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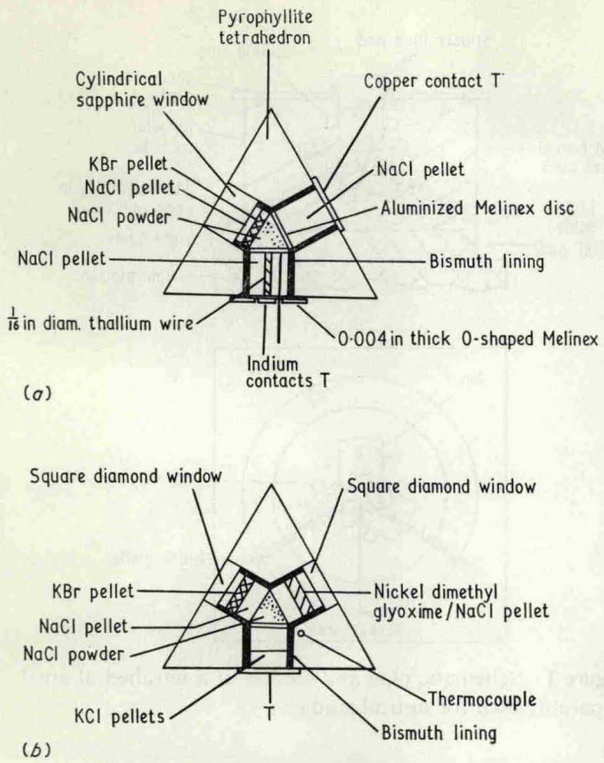

Figure 2 Schematic diagrams of tetrahedra that were used (*a*) for the determination of the bismuth and thallium calibration points, and (*b*) for the $Ni(DMG)_2$ optical calibration of the pressure

which are connected in parallel (see figure 1). The air is precooled in a series of heat exchangers using dry ice and liquid nitrogen. After passing through the cooling rings the cold air is allowed to circulate in the cone region before passing back through the initial counterflow heat exchanger. Little can be done to insulate the cone and anvil system thermally, and in consequence the consumption of dry ice and liquid nitrogen is large. Specimen temperatures within the tetrahedron as low as 100 K can be achieved and held constant to ± 5 K for several hours. Temperature measurements are made using a Chromel–Alumel Thermocoax which passes into the tetrahedron through one of the gaskets between a pair of anvils.

In a measurement of optical absorption, light from a 150 W quartz–iodine lamp is mechanically chopped at 800 Hz and focused on to the end of a 3·18 mm diameter light guide. The guide is bent so that the end protruding from the cone is horizontal, whilst the other end is adjacent to the high pressure window in the tetrahedron. Light emerging from the exit window traverses a second light guide and is then focused on to the entrance slit of a grating monochromator. The conventional exit slit of the monochromator may be replaced by an oscillating slit of constant width, the amplitude of vibration being variable. With the exit slit stationary, a transmission spectrum is recorded using a cooled photomultiplier and a conventional amplifier and phase-sensitive detector system. First and second derivative spectra are obtained by oscillating the exit slit and using the system adequately described elsewhere by Evans and Thompson (1969).

For work in the visible spectrum, commercially available incoherent multifibre glass guides were found to be excellent and preferable to single fibre guides. Although the latter have a greater intrinsic transmission, they suffer badly from surface damage as they are inserted into the cone and anvils. For work in the ultraviolet spectrum a Spectrosil quartz rod was coated by repeated vacuum evaporation with a uniform layer of LiF which in turn was covered with a layer of shellac for protection.

3 Pressure calibration at room temperature

A knowledge of the pressure acting on a sample for a given load is essential for the interpretation of high pressure experiments. For a tetrahedral anvil apparatus there is no simple 'force divided by anvil area' relationship, because of the unknown properties of the load that is supported by the gaskets. Also the compressibilities of the substances making up the volume of the tetrahedron have an important effect on the load–pressure relatonship (Lees 1966). The pressure calibration relies on the detection during each experiment of one or more of the phase transitions shown in table 1.

Table 1 Phase transitions of the materials used for pressure calibration

Phase transition	Associated physical change	Pressure characteristic of phase change (kbar)		Literature reference
		198 K	150 K	
KBr: FCC → BCC	10·5% volume decrease	17·9	19·5†	Bridgeman 1940
KCl: FCC → BCC	11% volume decrease	19·4	20·3†	Bridgeman 1940
Bismuth I → II	5% volume decrease 83% resistance decrease	25·3	NP	Il'ina and Itskevich 1966
Bismuth II → III	3% volume decrease 100% resistance decrease	26·8	NP	Il'ina and Itskevich 1966
Bismuth 'electronic'	—	NP	28·5	Il'ina and Itskevich 1966
Bismuth I → III	Resistance decrease	NP	32·3	Il'ina and Itsckevich 1966
Thallium II → III	1% volume decrease 30% resistance increase	37	?	Kennedy and La Mori 1962
Barium II → III	2% volume decrease 25% resistance increase	59·6	?	Kennedy and La Mori 1962
Bismuth V → VI	1·5% volume decrease	81	?	Giardini and Samara 1965

† Based on a linear extrapolation of data at higher temperatures. NP, transition not observed under the conditions quoted. ?, no information appears to be available.